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THE SEPARATION OF TITANIUM AND ALUMINUM, WITH A NOTE ON THE SEPARATION OF TITANIUM AND IRON.[1]

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In attempting to separate titanium and aluminum it is usual to resort to that method which depends upon the action of the slightly acid solution of the sulphates when submitted to prolonged boiling. The faultiness of this method, however, becomes apparent when solutions of aluminum and titanium are compared as to behavior under the conditions. To secure the complete precipitation of titanium the excess of sulphuric acid must be kept small, while to prevent the deposition of alumina the acid must be more than enough to dissolve the same amount freshly precipitated as hydrate, in the cold. Thus, upon boiling solutions containing the equivalent of 0.06 gram of titanic oxide, 2.5 grams of free sulphuric acid, beside alkaline sulphates, in 800 cm.^{3} of water, it was found that at the end of an hour 0.003 gram of titanic oxide in one case, and 0.006 gram in another experiment, had escaped precipitation; but that, when the solution of titanium had first been precipitated by ammonia and then made just acid by sulphuric acid, every trace of dissolved titanium was thrown out on boiling. The experiment, on the other hand, of boiling a gram of alum—roughly speaking 0.1 gram of alumina—in 800 cm.^{3} of water shows almost immediately the deposition of some alumina,

[1] Communicated by the Author, from the Proceedings of the American Academy of Arts and Sciences.

and the same thing happens when the alumina is first precipitated by ammonia and then dissolved by just enough sulphuric acid to effect the solution. The difficulty of so adjusting the acidity of the solution that no alumina shall be deposited and no titanium held up, is obvious. Test paper is of no aid in the case, since the reaction of alum itself and aluminic sulphate is acid. Under the circumstances it is hardly surprising that Knop[1] should revert from the troublesome, and only under remote conditions more exact, method of separation by boiling, to the convenient but indubitably inaccurate process of parting by the use of sodic hydrate. Knop employs both the dry and the wet method,—the fusion of the oxides in sodic hydrate, and the treatment of the salts in solution with sodic hydrate in excess; but both had long before been generally discarded, and the single experiment of acidulating the alkaline filtrate from a precipitate obtained by the treatment of a pure titanium salt according to either mode, and then making alkaline with ammonia, is enough to prove their worthlessness.

In an endeavor to secure a better means of separating titanium from aluminum I have followed two lines of experimentation; the one based upon the observation that, under properly controlled conditions, titanium is completely precipitated and alumina held in solution when an alkaline orthophosphate, strongly acidified with formic acid, is added to the solution of salts of these elements; the other, upon the solubility of alumina and the insolubility of titanic hydrate in sufficiently strong boiling solutions of acetic acid. Two preparations of titanium were used as test material in the course of the work; the solution of the fusion in sodic bisulphate of the hydrate precipitated by ammonia from the fluoride of titanium and potassium itself made from rutile and carefully purified by recrystallisation; and the solution obtained by treating the carefully prepared double fluoride with sulphuric acid, evaporating to dryness, redissolving in sulphuric acid and diluting with water. The second mode of preparation is the better, because the amount of alkaline sulphate present in the test solution is much smaller. At first, the strength of the solution was fixed by precipitating weighed amounts by ammonia, carefully washing, igniting and weighing the precipitate; but in the course of the work it became plain that the precipitation by means of ammonic acetate, or by ammonia with the

[1] Jahrb. f. Min. 1876, 756; Zeit. f. Kryst. u. Min. 1, 58.

subsequent addition of acetic acid in distinct excess, yielded more precise results. On this account, therefore, the determinations of the standard of the solutions employed in the later work were made by the acetic acid process, and the determinations by ammonia were corrected to correspond. In some of the experiments bearing upon this point, the results of which are given in the figures below, precipitations by ammonia were made in the cold and the liquid then heated to boiling; in those in which acetic acid was used just in excess, this reagent succeeded the ammonia at once, and the boiling followed; when precipitation was effected in presence of large amounts of acetic or formic acid, the acid was added in the amount intended, sodic acetate in quantity more than that necessary to decompose the sulphates present was introduced, and the clear solution heated to boiling, and kept boiling for a minute or two. The acetic acid employed was the C. P. article of commerce, and contained thirty-five per cent. of absolute acid. The amounts of it used—20 per cent., 30 per cent., 40 per cent., 50 per cent. by volume—correspond to 7 per cent., 10.5 per cent., 14 per cent., 17.5 per cent. of absolute acid. The formic acid contained twenty-seven per cent. of pure acid, and when it is said that there was in solution 5.4 per cent. of it, the absolute acid is meant; but it was the weaker acid, to the amount of 20 per cent. of the entire volume, which was actually used. The experiments were made in sets, and so appear in the record, in consequence of changes (due to slight depositions from time to time) in the strength of the test solution, which necessitated redeterminations of standard.

	Weight of Solution.	TiO_2 found.	TiO_2 in 50 grams.	Mode of Precipitation.
(1)	52.7370 grams.	0.3177 gram.	0.3012 gram.	By ammonia.
(2)	52.7610	0.3180	0.3012	
(3)	52.7620	0.3076	0.2912	By ammonia and excess of acetic acid.
(4)	41.8010	0.2436	0.2914	
(5)	52.9420	0.3381	0.3193	By ammonia.
(6)	53.0200	0.3384	0.3191	
(7)	10.6300	0.0667	0.3137	By acetic acid 7 per cent. by volume.
(8)	10.6960	0.0671	0.3137	
(9)	21.1030	0.1285	0.3044	By ammonia.
(10)	21.1480	0.1290	0.3049	
(11)	21.0810	0.1248	0.2960	By acetic acid 14 per cent. by volume.
(12)	21.1670	0.1259	0.2974	

	Weight of Solution.	TiO_2 found.	TiO_2 in 50 grams.	Mode of Precipitation.
(13)	21.0620 grams.	0.1270 gram.	0.3015 gram.	By ammonia.
(14)	21.2310	0.1279	0.3012	
(15)	10.4370	0.0617	0.2956	By acetic acid 10.5 per cent. by volume.
(16)	10.6590	0.0629	0.2950	
(17)	10.4870	0.0618	0.2946	By acetic acid 14 per cent. by volume.
(18)	10.8820	0.0637	0.2940	
(19)	10.4700	0.0615	0.2938	By formic acid 5.4 per cent. by volume.
(20)	10.7410	0.0627	0.2919	
(21)	52.3960	0.3396	0.3230	By ammonia.
(22)	52.4140	0.3378	0.3222	
(23)	52.6350	0.3340	0.3262	
(24)	52.5600	0.3372	0.3208	By acetic acid in distinct excess.
(25)	52.4830	0.3366, 0.3363	0.3207 0.3204	
(26)	52.3700	0.3348	0.3196	By acetic acid 17.5 per cent. by volume.
(27)	52.6420	0.3374	0.3205	

It will be noticed in the examination of these figures that parallel determinations usually agree very closely. The amounts of titanic oxide indicated by those experiments in which the precipitation was made by ammonia, are much in excess of those in which acetic acid was added subsequently. Thus the difference between (1), (2) and (3), (4) amounts to more than three per cent. of the total amount of the former; that between (5), (6) and (7), (8), to a little less than two per cent.; that between (9), (10) and (11), (12), to about two and a half per cent.; and a correction of more than two per cent. must be applied to (13), (14) to bring them to correspondence with (15), (16), (17), (18). The difference between (21), (22), (23) and (24), (25), (26), (27) is about one per cent., and the smallness of this figure in comparison with the differences previously noted is apparently explicable by the fact that the solution of titanium employed in the last determinations was prepared by the second of the methods mentioned above, and carries a smaller amount of alkaline sulphate. The tendency of titanic hydrate to include the sulphates of the alkalies is not strange in view of the well-known conduct of aluminic hydrate under similar circumstances, but the amount thus held is rather surprising. The experiments in which different proportions of free acid were introduced go to show, very strikingly, that, if acetic acid exerts any solvent action whatever upon the precipitate

thrown down by boiling the acetate, that action is very slight. Thus, between the mean of (24), (25) and that of (26), (27)—the one set precipitated by ammonia and treated before boiling with just a distinct excess of acetic acid, the other pair thrown out of a large volume, 700 cm.^{3}, one-half of which was acid of 35 per cent. strength, by boiling—we find a difference of but 0.0007 gram, and between the mean of (15), (16) and that of (17), (18), the difference (magnified five times by reference to 50 gram portions) is 0.0010 gram. In (25), too, we have an experiment in which the weighed precipitate was fused in sodic carbonate, dissolved, and again precipitated as before and weighed, the two weights differing by 0.0003 gram. Moreover, the filtrates from the precipitates thrown out in presence of an excess of acetic acid, when neutralised with ammonia, failed invariably to show the smallest precipitate, and in direct experiments upon the sensitiveness of the reaction it was found that on the addition of 0.0005 gram of titanic oxide in solution to 100 cm.^{3} of 35 per cent. acetic acid carrying a little sodic acetate, a distinct precipitate appeared almost immediately on boiling. It is plain, therefore, that so far as concerns the purpose in hand, the insolubility of the titanium precipitate in acetic acid may be taken as absolute. The small apparent losses to be observed in some of the determinations in which a large excess of acetic or formic acid was employed, are probably explicable by the tendency of the precipitate to change its consistency as the amount of free acid increases, and, in very acid solutions, to show an inclination to adhere in small amounts, but quite persistently, to the vessel in which precipitation takes place. The adherent precipitate may be dislodged with ease by putting a little hydrochloric acid into the beaker to which the precipitate adheres, covering and heating gently so that the acid volatilised may condense upon the walls of the beaker and again run down. By then rubbing the walls of the beaker a little and adding ammonia in excess, the trace of residual titanium is completely recovered. This method of recovery was applied in (26) and (27).

In preliminary experiments upon the first of the methods which seemed to promise a separation of titanium and aluminum, it was found that the precipitation of titanium by an alkaline orthophosphate is complete in the presence of a large amount of acetic or formic acid, and that, in the cold, and under conditions otherwise properly controlled, aluminic phosphate fails to appear. To

hold up the alumina by means of acetic acid requires some care in the adjustment of the acid and phosphate, and to redissolve the precipitate once formed is a matter of considerable difficulty. Thus, to clear the solution of a precipitate produced by 1.5 grams of the phosphate of soda and ammonia upon 0.1 gram of alumina, it was necessary to dilute the liquid to a volume of 250 cm.^{3}, and add acetic acid until there was in the solution at least five per cent. of absolute acid; and the addition of 1.5 grams more of the precipitant again precipitated aluminic phosphate. Formic acid, however, is more active, and the balance between it and the precipitant not so delicate. When the proportion of three parts by weight of absolute formic acid to two parts of microcosmic salt is kept, the aluminic phosphate does not fall; and if, because of a deficiency of acid, precipitation does not take place, the liquid immediately clears so soon as the proportion of acid and precipitant is restored. Formic acid, therefore, was used in the experiments about to be described. The test solution of titanium was that employed in the previous experiments (1) to (20), but, inasmuch as the error of the process had not yet been remarked, the standards were determined by precipitating by ammonia, and are therefore to be corrected. The application of a correction of two and a half per cent. to the apparent weights of titanic oxide found by the ammonia process —the mean correction for (1), (2), (5), (6), (9), (10), (13), (14)— cannot lead far away from the truth, since the difference between the maximum and minimum corrections observed amounts for the quantity of material employed in these experiments to but 0.0002 gram. Determinations of standard, original and corrected, are given in (28), (29), (30), and (31).

	Weight of Solution.	TiO_2 found.	Corrected TiO_2 in 50 grams.	Corrected TiO_2 in 50 cm.^{3}
(28)	52.7660 grams.	0.3867 gram.	0.3572 gram.	0.3771 gram.
(29)	52.8410	0.3869	0.3569	
(30)	52.5380	0.3810	0.3627	
(31)	52.6920	0.3822	0.3627	

A portion of the solution, the standard of which is set by (28) and (29), was diluted to ten times its volume, and 50 cm.^{3} of the diluted solution were used in each of the experiments immediately following. These were made to determine whether the precipitate was definite in composition, and might be weighed as such. Precipitation was effected by a solution of microcosmic salt acidified with formic acid. The precipitates of (32) and (33) were collected

on paper, that of (34) on asbestos, and all were ignited and weighed directly.

	Amount taken.	TiO_2 and P_2O_5 found.	TiO_2 by Standard.	P_2O_5 by Difference.
(32)	50 cm.³	0.0731 gram.	0.0377 gram.	0.0354 gram.
(33)	"	0.0640	0.0377	0.0263
(34)	"	0.0753	0.0377	0.0376

The phosphate obtained by Merz[1] by precipitating in presence of hydrochloric acid containing two molecules of TiO_2 to one of P_2O_5, requires 0.0326 gram of P_2O_5 to 0.0377 gram of TiO_2. It will be noticed that in two determinations the P_2O_5 is in a considerable excess of the amount demanded by this proportion, and in one, in deficiency. The idea of weighing the phosphoric anhydride and titanic oxide together was therefore abandoned.

In experiments (35), (36), (37), the titanium was present alone; in (38), (39), 2 grams of alum were added to the solution before precipitating by means of the mixture of microcosmic salt and formic acid, 5 grams of the former being employed to 8 grams of the latter. The precipitates of all, excepting (35), were carefully washed, ignited, fused with sodic carbonate, and the product of fusion was dissolved in water, the insoluble titanate separated from the soluble phosphate by filtration and washing, ignited, again fused with a little sodic carbonate, the result of fusion dissolved in strong sulphuric acid, diluted with water, and precipitated by ammonia with the subsequent addition of acetic acid, and boiling. Experiment (35) was conducted in like manner, excepting that the sodic titanate was dissolved off the filter by means of a mixture of hydrochloric and oxalic acids, the latter destroyed by potassic permanganate (since there is danger that in presence of ammonic oxalate the titanium may not be completely precipitated by ammonia), ammonia added in excess, then acetic acid to strongly acid reaction, and the liquid boiled. This mode of treating the acid titanate is not desirable, since the titanic hydrate, if precipitated but once subsequently, retains a trace of manganese. To fuse the titanate with sodic carbonate, and then treat the melt with strong sulphuric acid, is probably the best way of getting the titanium into solution again. The test solution of (28) and (29) was employed in experiment (35), and that of (30) and (31) in the rest.

From experiments (36) and (37), together with (35), which, as has been remarked, would naturally give figures slightly too high,

[1] Jour. prakt. Chem. **99**, 157.

it appears that the method indicates with accuracy the amount of titanium present. Experiments (38) and (39) indicate that the separation from alumina is not unreasonably inexact.

	Weight of Solution.	TiO_2 found.	TiO_2 by Standard.	Error.
(35)	5.2220 grams.	0.0383 gram.	0.0373 gram.	0.0010 gram +
(36)	5.2300	0.0371	0.0370	0.0001 +
(37)	5.3840	0.0380	0.0381	0.0001 —
(38)	5.2920	0.0367	0.0374	0.0007 —
(39)	5.2540	0.0383	0.0372	0.0011 +

The tediousness of filtration, which is a consequence of the nature of the phosphate precipitate, is the great objection to the method, and on account of it the testing was pushed no further, attention being turned instead to the second line of experimentation.

The incompleteness of the precipitation of alumina by the basic acetate process in presence of a large excess of acetic acid, suggested the attempt to hold up alumina entirely by means of a sufficient excess of acetic acid while precipitating titanium. Experiments to determine the amount of acetic acid necessary to prevent the precipitation of alumina from a boiling solution of the acetate, indicate that amounts of absolute acid in excess of five per cent. by volume of the solution are adequate to the purpose, and that the addition of sodic acetate in reasonable amounts does not sensibly affect conditions. It appears, further, that the addition of a very small quantity of titanium in solution to the clear boiling solution of alumina in acetic acid occasions at once a perceptible precipitation. Thus, 0.0005 gram of titanic oxide in solution produced a distinct and appreciable opalescence in 500 cm.^{3} of liquid containing 10 grams of alum, 15 grams of sodic acetate (about twice the amount necessary to convert the sulphate of alumina to the acetate), and seven per cent. by volume of absolute acetic acid.

In respect to holding up alumina, formic acid acts like acetic acid, but more potently.

In the following experiments to test the method quantitatively, two solutions of titanium were employed: in (40) and (41), the solution the value of which was fixed by (15) to (18); in (42) to (46), the solution whose standard was set by (24) to (27). To the cold solution of titanium containing a little free sulphuric acid together with some alkaline sulphate were added 5 grams of alum

(approximately 0.5 gram of alumina), 20 grams of sodic acetate, which was always more than enough to effect the entire conversion of the aluminic and titanic sulphates to acetates, acetic acid to such amount that in experiments (42), (43), (44) there should be in the solution seven per cent. by volume of absolute acid, and in the remaining experiments ten and a half per cent. by volume, and water to make the entire volume 250 cm.^{3} in (40) and (41), and 400 cm.^{3} in the rest. The clear solutions obtained in this manner were raised quickly to boiling, kept at that point for a minute, and removed from over the burner so that the precipitate might settle, as it does almost immediately. The supernatant liquid was decanted upon a filter sufficiently porous to permit very rapid filtration,[1] and the precipitate added immediately thereafter, and washed with 7 per cent. acetic acid followed finally by hot water. The washed precipitate was dried, ignited and weighed. The precipitate once upon the filter and drained becomes more compact and easily washed, and strong ignition of fifteen or twenty minutes over a good Bunsen burner, after the paper is thoroughly ashed, reduces it to a weight which neither the blast-lamp nor ignition in an atmosphere of ammonic carbonate changes.

	Weight of Solution.	TiO_2 found.	TiO_2 by Standard.	Error.	
(40)	10.4910 grams.	0.0645 gram.	0.0618 gram.	0.0027 gram	+
(41)	10.5970	0.0656	0.0624	0.0032	+
(42)	20.9520	0.1450	0.1343	0.0107	+
(43)	21.1750	0.1439	0.1357	0.0082	+
(44)	21.0250	0.1431	0.1347	0.0084	+
(45)	20.8740	0.1393	0.1338	0.0055	+
(46)	21.0570	0.1402	0.1349	0.0053	+

It is quite obvious that a single precipitation by the method used does not yield titanic oxide free from alumina. The weighed precipitate of each experiment was therefore fused with a small quantity of sodic carbonate, and the product of fusion treated in the crucible with strong sulphuric acid, which gradually with the aid of gentle heat dissolved everything completely. This solution after cooling was poured directly into 100 cm.^{3} of cold water, and, the liquid remaining clear, ammonia was added just to alkalinity, and then dilute sulphuric acid corresponding to 2.5 grams of pure

[1] The paper No. 589 of Schleicher and Schüll is excellent for the purpose.

acid. The precipitate thrown down by ammonia was gradually, but after a few minutes entirely redissolved, acetic acid was added until it amounted in terms of absolute acid to ten and a half per cent. of the entire volume, 20 grams of sodic acetate introduced, the solution boiled, and the precipitate treated as previously described. The results of this second treatment are given below.

	Weight of Solution.	TiO_2 found (II).	TiO_2 by Standard.	Error.
(40)	10.4910 grams.	0.0624 gram.	0.0618 gram.	0.0006 gram +
(41)	10.5970	0.0623	0.0624	0.0001 —
(42)	20.9520	0.1373	0.1343	0.0030 +
(43)	21.1750	0.1385	0.1357	0.0028 +
(44)	21.0250	0.1369	0.1347	0.0022 +
(45)	20.8740	0.1357	0.1338	0.0019 +
(46)	21.0570	0.1383	0.1349	0.0034 +

In experiments (40) and (41), in which comparatively small amounts of titanium were employed, the separation from alumina was reasonably good after the second precipitation, but in (42) to (46) the larger quantities of titanic oxide still retained notable amounts of alumina. The precipitates of (45) and (46) were, therefore, treated again just as before, to determine the effect of a third precipitation.

	Weight of Solution.	TiO_2 found (III).	TiO_2 by Standard.	Error.
(45)	20.8740 grams.	0.1347 gram.	0.1338 gram.	0.0009 gram +
(46)	21.0570	0.1360	0.1349	0.0011 +

Three precipitations left the titanic oxide of these experiments nearly free from alumina, but three such treatments involve a good deal of labor, and, moreover, it is evident that the precipitate still holds with tenacity traces of alumina. The experiment of attempting to remove residual alumina after a single precipitation, by treating the product of fusion of the precipitate in sodic carbonate with boiling water, filtering, igniting the residue, again fusing with a little sodic carbonate, and proceeding from this point to dissolve in sulphuric acid and precipitate once more as before, was therefore tried, and the result is given in the record of (47) to (50).

	Weight of Solution.	TiO_2 found.	TiO_2 by Standard.	Error.
(47)	20.8640 grams.	0.1329 gram.	0.1337 gram.	0.0008 gram —
(48)	21.1100	0.1345	0.1354	0.0009 —
(49)	20.9100	0.1332	0.1340	0.0008 —
(50)	21.0020	0.1348	0.1346	0.0002 +

This mode of treatment appears to remove the last traces of alumina, and yields a reasonably good separation.

It appears, therefore, to recapitulate, that for the separation of titanium and aluminum either of the processes set forth in the preceding work may serve. The first, however, which is, in brief, the treatment of the solution containing salts of the elements in question with a mixture of microcosmic salt and formic acid, in the proportion of two to three by weight, together with enough ammonic formate to take up the stronger acids, fusing the precipitate in sodic carbonate, extracting with water, fusing the residue in a small amount of sodic carbonate, dissolving in sulphuric acid and precipitating by ammonia with the subsequent addition of acetic acid, and boiling—though probably fairly accurate, is, on account of the nature of the precipitated phosphate, not comparable with the second method in point of convenience. The latter process, which involves many different manipulations—the introduction into the solution of titanium aud aluminum of enough acetic acid to make from seven to eleven per cent. by volume of the absolute acid, together with sufficient sodic acetate to fix all of the stronger acids in sodium salts, boiling, filtering and washing with acetic acid of seven per cent. strength, fusing the ignited precipitate in sodic carbonate, extracting with boiling water, again fusing the residue with a little sodic carbonate, dissolving in strong sulphuric acid and pouring this solution into water, neutralising with ammonia, redissolving the precipitate in a known amount of sulphuric acid, and precipitating finally by boiling with acetic acid and sodic acetate as at first—and appears in the description to be long and tedious, may in reality be carried out with ease and rapidity, the operations being generally short and not of a difficult nature.

In most cases in which titanium is to be separated from aluminum, it is necessary to effect the removal of iron as well. Some experiments looking to the separation of titanium and iron, by boiling the acetates in presence of a large excess of acetic acid, were unsuccessful; for, though an excess of acetic acid amounting to eleven per cent. of absolute acid in the solution is enough to prevent the deposition of a basic ferric acetate, it appears, unexpectedly, that in presence of ferric acetate in solution the titanium shows a very marked tendency to remain dissolved. Thus, an amount of iron alum the equivalent of 0.2 gram of ferric oxide, together with 10

grams of sodic acetate and seventeen per cent. of absolute acetic acid, in a total volume of 400 cm.³, held 0.06 gram of titanic oxide completely in solution during boiling prolonged a quarter of an hour. In an experiment the counterpart of this, excepting only the addition of sodic acetate, the titanium began to deposit at once on boiling; and Streit and Franz,[1] in proposing the ebullition of the sulphates in presence of a large excess of acetic acid as a means of procuring titanic oxide free from iron, claim a complete precipitation under these conditions. The behavior of the sulphates of titanium and zirconium when in solution together appears to be analogous to this action of the acetates of iron and titanium, and iron in the ferric condition is generally supposed to influence somewhat the precipitation of titanium from the solution of the sulphates.

When iron and titanium appear together in solution, and are to be separated, the choice lies between Stromeyer's application of Chancel's hyposulphite method,[2] which yields milky filtrates,—always undesirable,—and that process which involves the precipitation of iron by ammonic sulphide in presence of ammonic tartrate to hold up the hydrates which would be precipitated in its absence. This latter method has been regarded as an undesirable one, chiefly on account of the inconvenience involved in the evaporation of the filtrate from the ferrous sulphide and the ignition of the residue to remove the tartaric acid, and so to permit the recovery of the bases. The difficulty in question may be obviated, however, by destroying the tartaric acid by potassic permanganate added gradually to the hot solution containing enough free sulphuric acid to leave some excess after the conversion of all the permanganate. The oxidation of tartaric acid by potassic permanganate does not, as is well known, yield carbonic acid and water alone, but gives rise also to a considerable quantity of formic acid as an intermediate product. When the permanganate begins to act upon the formic acid, the oxidation, going more slowly, results in the deposition of a brown manganic hydrate, which, if any tartaric acid remains in solution, redissolves quite rapidly, and in presence of formic acid as the only reducing agent, more slowly. When, therefore, manganic hydrate is abundantly precipitated in the boiling solution, and does not perceptibly dissolve, it is quite certain that the conversion of the tartaric acid to formic acid—which is all that is needed in this case—has been accomplished;

[1] Jour. prakt. Chem. **108**, 65. [2] Ann. Ch. Pharm. **113**, 127.

but for the sake of greater security the addition of permanganate may be continued until its color shows in the solution. It is well, however, to make use in this process of a known amount of tartaric acid,—experience has shown that an amount equal to three times the weight of the oxides to be held in solution is sufficient, unless ammonia be used in enormous excess and the boiling prolonged,—and to employ for its destruction two and a half times its own weight of potassic permanganate, this quantity being more than enough to carry the oxidation to the final products, providing there were no deposition of manganic hydrate. The manganese thus introduced into the solution may be removed by two acetate precipitations, which, if alumina is to be separated, must be made at any rate, even if no manganese be present.

To separate titanium, aluminum and iron, therefore, I find it most convenient to precipitate the iron by passing hydric sulphide into the faintly ammoniacal solution of the oxides in ammonic tartrate, taking care that the solution is still ammoniacal just before filtering; to destroy the tartaric acid in the filtrate, after acidifying and boiling off the hydric sulphide by means of potassic permanganate in the manner just described, redissolving residual manganic hydrate by the addition of a little ammonic bisulphite, and boiling off the excess of sulphurous acid; and to separate the titanium and aluminum by the acetate process.

A single point in the analysis of silicates may be worthy of note in this connection. If phosphoric acid be present, as is often the case, the separation of titanium from silica by the action of cold water upon the product of fusion in sodic or potassic bisulphate is liable to uncertainty, on account of the formation of the insoluble titanic phosphate which remains partly with the silica and in part clouds the filtrate. The siliceous residue should, therefore, be treated with sulphuric and hydrofluoric acids to recover titanium which may be with the silica. It is better in most cases to effect the decomposition of a silicate by means of one of the fluoride methods, or by fusion in an alkaline carbonate, the melt in the latter case being acidified with hydrochloric acid, and the residue after evaporation and filtration worked over with sulphuric and hydrofluoric acids for the recovery of that portion of the titanium which remains insoluble after the evaporation.

A NEW METHOD FOR THE DETERMINATION OF PHOSPHORUS IN IRON AND STEEL.[1]

By J. B. Mackintosh.

The general method which has been followed since the time of Heinrich Rose, and perhaps before, for the determination of phosphorus in iron and steel, is to dissolve the sample either in nitric acid, *aqua regia*, or some other oxidising agent, in order to convert the phosphorus into phosphoric acid.

In 1832 Rose[2] recommends HNO_3, or *aqua regia*, preferably the former. Wöhler, in 1854,[3] directs that the iron should be oxidised by burning in a stream of oxygen for the determination of carbon, and the resulting oxide of iron containing all the phosphorus as phosphoric acid be treated as an ore. In the fourth English edition of Fresenius' Quantitative Analysis,[4] pp. 666–667, we find directions to dissolve the iron in *aqua regia* or bromine; and, coming down to more recent times, we find F. A. Cairns[5] directing the employment of a boiling solution of potassium chlorate and hydrochloric acid for the oxidation and solution of the sample to be analysed. It is unnecessary to multiply quotations from the literature of the subject, though they might be extended almost indefinitely, since it would only be a repetition of the above-mentioned series of methods in one form or another; and the references given have been selected to show how little essential variation there is in the type-methods of solution used. In fact it seems to be universally accepted as a necessary first step in the determination that some such method of solution should be followed.

One chemist, however, struck out on a different line of thought, and to the best of my knowledge only one, M. V. Tantin, who, in a contribution to the Comptes Rendus (I have not been able to find the original article, however), copied in the Chemical News,[6]

[1] Communicated by the Author, from the Transactions of the American Institute of Mining Engineers.

[2] Rose's Traité Pratique d'Analyse Chimique. Translated from the second German edition, by A. J. L. Jourdan, 1832, **2**, 414.

[3] Wöhler's Handbook of Inorganic Analysis. Edited by A. W. Hofmann. London, 1854, 61.

[4] 1865. [5] A Manual of Quantitative Chemical Analysis. By F. A. Cairns, A. M., 1880, 114.

[6] Chemical News **18**, 252.

describes his method for determining phosphorus in cast-iron as follows:

"When seeking the means of avoiding these sources of error,[1] I concluded that the best way of so doing would be to use a precisely contrary method; namely, by liberating the phosphorus as a hydrogen compound; but one objection naturally arose—would the totality of the phosphorus pass into the state of a gaseous product? I may safely affirm that I have never been able to discover the least trace of phosphorus in the residue after the complete attack of the cast-iron by chlorhydric acid, which fact is not surprising if it be considered what strong affinities phosphorus has for hydrogen."

According to M. Tantin, the resulting gases, composed of phosphuretted, arsenuretted, sulphuretted, and carburetted hydrogen, are passed through potash and then into nitrate of silver, where all the phosphuretted hydrogen is caught as phosphide of silver, which is afterwards treated with *aqua regia*, and the phosphoric acid resulting determined as ammonic-magnesic phosphate. The following precautions are mentioned as indispensable.

1. The cast-iron must be attacked very slowly, or part of the phosphuretted hydrogen may traverse the solution of nitrate of silver without being absorbed.

2. When the solution is finished, a current of hydrogen is to be passed through the apparatus.

M. Tantin seems to have overlooked the possibility of some of the phosphorus remaining in the solution, and to have assumed that if none was found in the residue, all must have gone off with the gas. If such were the case, the determination of phosphorus would be much simplified.

Some years ago I tried this method on a pig-iron which I knew contained over one per cent. of phosphorus, but my final precipitate, if any, of ammonic-magnesic phosphate was so small as to be invisible. I concluded that the method was not suited for American pig-irons, and gave no more attention to the subject till the present summer, during which I have had considerable leisure time for experiment.

In Watts's Dictionary of Chemistry[2] we find the statement, "When a very small quantity of phosphorus is associated with a

[1] Loss as phosphuretted hydrogen; estimation of arsenic as phosphorus; and errors due to large bulk of solutions employed.

[2] 1866, 4, 519.

large quantity of iron, as in many kinds of pig-iron, the whole dissolves in hydrochloric or dilute sulphuric acid, the phosphorus passing into solution as phosphoric acid." This statement is the very reverse of that made by M. Tantin, and to ascertain its accuracy I made the following experiment.

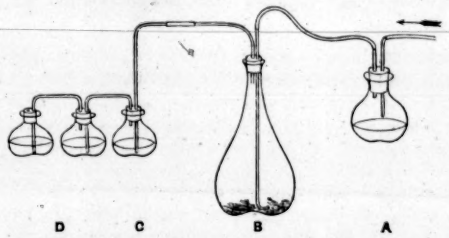
I had just finished an analysis of bar-iron which, by the ordinary method I used,[1] had given 0.124 per cent. phosphorus. I took 10 grams of this and dissolved it in hydrochloric acid, finally boiling the solution; neutralised with ammonia, and after adding a few cc. of permanganate to oxidise a little iron, precipitated basic acetates, boiling the filtrate twice for further precipitates; the combined precipitates were dissolved in hydrochloric acid, oxidised with nitric acid, precipitated with ammonia, and the precipitate redissolved in nitric acid, and the phosphorus precipitated with ammonium-molybdate, finally weighing the yellow precipitate. The result I obtained by this method was 0.122 per cent., which is a very satisfactory confirmation of the statement the experiment was meant to verify. The time taken in this determination was about from 5 to 6.30 P. M. one evening, by which time I had the yellow precipitate formed,[2] and the time necessary to filter and weigh the precipitate the next day, perhaps an hour more.

This result being so satisfactory, I treated some filings of a high-phosphorus pig (in which by my ordinary method I had found 0.826 per cent.) in the same manner, but found that I had only succeeded in obtaining 0.580 per cent., or about five-sevenths of the total amount present. I also prepared a button of very high-phosphorus iron, and on treating in the same way found that I only obtained about three-quarters of the amount present. This made me think that probably the loss was due either to the escape of phosphuretted hydrogen or to the formation of some other compound than phosphoric acid. I therefore arranged a simple apparatus, the same, in fact, which I use for the determination of sulphur in iron, which is filled with an atmosphere of hydrogen

[1] Ten grams dissolved in 120 cc. nitric acid sp. gr. 1.20, evaporated to dryness and heated in air-bath to 120° to 130° C. several hours, redissolved in hydrochloric acid, reduced with ammonium bisulphite: precipitate the phosphoric acid by a basic acetate separation, boil the filtrate twice for further precipitates, making three in all, dissolve the combined precipitates in hydrochloric acid, filter out silica, oxidise solution with nitric acid, precipitate with ammonia, redissolve the precipitate in nitric acid, and ammonic molybdate. This last precipitate is redissolved in ammonia and reprecipitated by nitric acid, is then filtered on a Gooch crucible, dried and weighed, and afterwards checked by precipitation as ammonic-magnesic phosphate.

[2] I did not seek to remove silica by evaporation to dryness. Per cent. Si = 0.151.

throughout the operation, and consists of a flask A to hold the acid, a flask B for the iron, and flasks C and D, of which C is generally left empty to catch condensed steam, and the two flasks D contain the absorbent liquid.



The absorbent liquid in D was a solution of potassium-permanganate acidified with nitric acid. The iron having been placed in B, and the necessary amount of dilute hydrochloric acid to dissolve it in A, the whole apparatus was filled with hydrogen, a current of which was kept passing through the whole time. When the air was all expelled the flask A was inverted above the level of B, so that its contents flowed into B, and the solution of the iron commenced. The solution was heated to boiling for some minutes, and when all had dissolved, with the exception of the insoluble portion, the apparatus was disconnected, the insoluble residue filtered from the solution, the solution divided into equal parts, one of which was oxidised with nitric acid and treated as in an ordinary determination of phosphorus, while the other was immediately precipitated by basic acetate, as in the first experiment described.[1] The amounts of phosphorus found in the prepared iron phosphide were distributed as below.

In residue, ...		3.79 per cent.	
In solution	oxidised with nitric acid,	2.66	
	basic acetate direct,		2.16 per cent.
In gas, ...		0.05	
		6.50	

[1] Care being taken to remove silica wherever present.

Showing a loss of 0.50 per cent. of phosphorus in the solution in some other form than phosphoric acid. It is very possible that nitric acid fails to oxidise to phosphoric acid all the phosphorus compounds formed in the solution. Referred to the total amount of phosphorus found (6.50 per cent.), the distribution per cent. is as follows:

In residue,	58.31
Recovered from basic acetate precipitation,	33.23
Lost,	7.69
In gas,	0.77
	100.00

I repeated the above process on a sample of pig-iron said to contain 0.885 per cent. phosphorus, and in which, by my usual method, I found 0.880 per cent. weighing as magnesia pyrophosphate, or, calculating from the weight of the yellow precipitate, 0.878 per cent. This was also conducted in a hydrogen atmosphere. The gas was caught in permanganate acidified with sulphuric acid in the first flask and with nitric acid in the second. Nearly all the phosphorus in the gas was retained in the first flask, a very small amount only passing over to the second. The results obtained were,

Phosphorus in residue,		0.345 per cent.
In solution	basic acetate precipitate,	0.451
	lost,	0.065
In gas,		0.019
		0.880

The distribution of the phosphorus is,

In residue,		39.11 per cent.
In solution	basic acetate precipitate,	51.13
	loss,	7.60
In gas,		2.16
		100.00

I then took a sample of high-phosphorus pig in which I had found in the usual way, 1.45 per cent. (weighed as yellow precipitate), or 1.48 per cent. (weighed as magnesia pyrophosphate), and dis-

solved 1 gram in 10 cc. hydrochloric acid and 30 cc. water, finally heating the solution to boiling. This time, instead of a stream of hydrogen being passed through the apparatus, a stream of oxygen was employed. The escaping gas was passed through permanganate and nitric acid. All the phosphorus caught was found in the first flask.

The residue, as in all these experiments, was heated with nitric acid and potassium chlorate; the solution was partially oxidised with 10 cc. permanganate (1 cc.=.01 Fe), and precipitated as basic acetate as usual; the silica separated from both portions, and the phosphorus determined. The total amount of phosphorus found was 1.42 per cent. weighed as magnesia pyrophosphate, or 1.37 per cent. weighed as the yellow precipitate, showing a loss of 0.06 per cent. The distribution of the phosphorus was,

In residue,		37.47 per cent.
In solution	basic acetate precipitate,	55.20
	loss,	4.05
In gas,		3.28
		100.00

I next took 2 grams of the .880–.885 per cent. pig, and dissolved it, as in the last case, in a stream of oxygen, but instead of following up each portion separately, mixed them all together (the gas was caught in sulphuric acid permanganate), and collected the residue with the first basic acetate precipitate, treated with nitric acid and potassium chlorate, and proceeded as before. The phosphorus found was only 0.771 per cent., or of the total amount present, 87.41 per cent. was found and 12.59 per cent. lost.

I repeated the last experiment, using, however, dilute sulphuric acid in place of hydrochloric as the solvent, a stream of oxygen passing continually through, and the solution being kept boiling for fifteen minutes after all visible action had ceased. The total phosphorus found was 0.767 per cent., distributed as follows:

In residue,		14.17
In solution	basic acetate precipitate,	70.86
	loss,	13.16
In gas,		1.81
		100.00

These last two experiments showed that oxygen was not sufficient to convert the phosphorus in the forms lost into phosphoric acid; so the problem resolved itself into finding a method of converting the lower oxygen compounds of phosphorus into phosphoric acid, without simultaneously oxidising ferrous to ferric iron. The solution of this problem was obtained in the next trial. The process is the same as before described, using hydrochloric acid as the solvent, and a current of oxygen;[1] and after raising the solution to boiling, introducing an excess of a strong solution of sulphurous acid previously placed in the flask A, and continuing the boiling for some minutes. The result of the reaction is visible in the precipitation of sulphur in the solution, and the insoluble residue is much altered in appearance, being much more disintegrated. The results obtained in this experiment were: total phosphorus present, 0.882 per cent., weighed as magnesia pyrophosphate (care being taken to ensure its purity by resolution and reprecipitation of the magnesia precipitate), distributed

In residue, ...	13.49 per cent.
In solution, ...	80.84
In gas, ...	5.67
	100.00
Loss, ...	0.00

In confirmation of this result I made another determination in the same manner, starting at noon; by the following morning I found 0.865 per cent. of phosphorus, and had lost a small amount in the course of the rather hurried analysis.

The results obtained are given in tabular form on the next page.

I also made some confirmatory experiments on the sample used in experiment No. 5, weighing the yellow precipitate first obtained, instead of purifying it by reprecipitation. The precipitates carried traces of iron, which in experiments 11 and 12 entered into the magnesia precipitates. This explains discrepancies observable between the results calculated from the weights of the yellow precipitate and from those of the magnesic pyrophosphate.

[1] The use of oxygen in place of hydrogen is recommended because it has no appreciable oxidising effect on the iron solution, while it prevents the reduction of the permanganate, which rapidly takes place with hydrogen.

Number.	Sample.	Per cent. P.	Method employed.	Per cent. P. found.			Total per cent. found.	Loss.	Per cent. distribution.			
				Residue.	Solution.	Gas.			Residue.	Solution.	Gas.	Loss.
1	Bar-iron, . . .	0.124	Sol. in HCl and direct basic acetate precipitation.	0.122		...	0.122	0.002	...	98.4	...	1.6
2	Pig, ...	0.826	Sol. in HCl and direct basic acetate precipitation.	0.580		...	0.580	2.46	...	...	...	...
3	Iron phosphide, .	6.50?	Sol. in HCl in H atmosphere. Gas absorbed in $K_2Mn_2O_8$ and HnO_3.	3.79	2.16	0.05	6.00	0.50	58.31	33.23	0.77	7.69
4	Pig, ...	0.880	Sol. in HCl in H atmosphere. Gas in $K_2Mn_2O_8$ + H_2SO_4.	0.345	0.451	0.019	0.815	0.065	39.11	51.13	2.16	7.60
5	Pig, ...	1.48	Sol. in HCl in O atmosphere. Gas in $K_2Mn_2O_8$ + HNO_3.	...	...	...	1.42	0.06	37.47	55.20	3.28	4.05
6	Pig, ...	0.880	Sol. in HCl in O atmosphere. Mixed all portions. Gas in $K_2Mn_2O_8$ + H_2SO_4.	...	...	...	0.771	0.109	...	87.41	...	12.59
7	Pig, ...	0.880	H_2SO_4 in O atmosphere and solution boiled 15 minutes.	...	...	...	0.767	0.111 gain.	14.17	70.86	1.81	13.16
8	Pig, ...	0.880	HCl in O atmosphere, boiled with excess SO_2.	...	...	...	0.882	0.002	13.49	80.84	5.67	0.00
9	Pig, ...	0.880	HCl in O atmosphere, boiled with excess SO_2, but all portions mixed.	...	...	...	0.865	0.015	Slight loss in course of analysis.			

Percentage P.	Old Method.	New Method.		
	No. 5.	No. 10.	No. 11.	No. 12.
Weighed as yellow precipitate, ...	1.447	1.49	1.451	1.463
No. of precipitations, . .	2	1	1	1
Weighed as $Mg_2P_2O_7$, .	1.480	1.456	1.516	1.539
No. of precipitations, . .	1	2	2	1

From inspection of this table it is seen that there is a far closer agreement between the results calculated from the weights of the yellow precipitate than in those calculated from the magnesic pyrophosphate; and I am of the opinion that the true percentage of this sample is very near 1.454, the average of the four lowest results obtained.

In experiment 10 the phosphorus found was distributed—

In residue, ...	23.10
In solution, ...	73.00
In gas, ...	3.90
	100.00

In experiments 11 and 12 all portions were mixed together.

The following is a brief outline of the steps to be followed:

1. Solution in hydrochloric acid in a stream of oxygen or air, absorbing the escaping gases in permanganate acidified with sulphuric acid.

2. Heating the solution to boiling, stopping the passage of the oxygen current, and carefully adding an excess of sulphurous acid solution, and continuing the boiling till the precipitated MnO_2 in the absorption-flasks is redissolved. This boiling should last several minutes to ensure the completion of the reaction.

3. Disconnecting the junctions between the absorption-flasks and solution-flask, and between the solution-flask and the acid-flask, and allowing to cool.

4. Mixing solutions, filtering out residue, which is placed (with filter paper) in a porcelain casserole, oxidising with nitric acid and potassium chlorate, and evaporating to dryness.[1]

5. Boiling the solution till the excess of sulphurous acid is expelled, adding a few cc. of permanganate to peroxidise a little of the iron, and precipitating basic acetates. Boiling the filtrate for other precipitates, to ensure getting all the phosphoric acid present.

6. Dissolving these precipitates in hydrochloric acid, and adding to the solution of the residue in which, by this time, the paper will have been thoroughly destroyed.

7. Evaporating to dryness for silica, and proceeding as usual with the molybdate precipitation.

The saving of time by this process is the greater, as the percentage to be determined is less. In a steel of low percentage, where it is necessary to use 10 grams for the determination, necessitating the use of 120 cc. of nitric acid for solution, by the old method, the time taken for the evaporation of this amount of liquid, for the subsequent thorough drying of the residue, and for the resolution and reduction of the iron to the ferrous state, is evidently much greater, and the operations followed are much more tedious than by this method, where the phosphorus is concentrated at the start in but a few milligrams of iron in very little bulk of solution, enabling the subsequent evaporation to dryness, and thorough drying of the residue to be performed in a very short period.

In M. Tantin's experiments he used cast-iron only. Mine have been conducted on pig and wrought-iron. It is possible that the difference in our results may be partially accounted for by different modes of occurrence of phosphorus similar to the different forms of carbon, but of this I cannot speak from experience, and merely offer it as a suggestion.

The small amount of phosphuretted hydrogen which is found seems to be the product of a secondary reaction between phosphorous acid and the nascent hydrogen evolved. Whether hypophosphorous or hypophosphoric acids are present, or, indeed,

[1] I prefer to filter out the residue instead of filtering it out with the first basic acetate precipitate, because it is difficult to work accurately on a muddy liquid, and because there is a probability of loss of phosphorus by the continued action of the hot acid solution on the residue, after the sulphurous acid has been expelled. By proceeding as directed, this chance of loss is removed. Perhaps some of the loss in the ninth experiment may be due to this cause, as the residue in that experiment was not separately treated.

whether phosphorous acid is present, I am at present unable to say, but the results obtained point to the presence in the solution, along with phosphoric acid, of one or more of these as the cause of loss. The use of sulphurous acid, however, oxidises these to phosphoric acid without affecting the iron, so that by this process a determination can be made in a day which formerly required several days.

In calculating the percentage of phosphorus from the weight of the yellow precipitate, I have used in all cases the figure of 1.63 per cent. phosphorus in the precipitate, and have thought it worth while to give the results I have obtained in two determinations I have recently finished. I prepared the yellow precipitate from phosphoric acid, precipitated in the usual manner with excess of molybdic acid. One of these precipitates (A) was purified from possible excess of molybdic acid by solution and reprecipitation; the other (B) was analysed without going through this process. The magnesia precipitate obtained from A was also purified by solution and reprecipitation, while that from B was ignited and weighed direct. The results are given below.

	A.	B.
Weight of yellow precipitate dried at 95°–100° C.	1.2802	1.1428
Weight of $Mg_2P_2O_7$, ...	.0735	.0664
Weight of P calculated from $Mg_2P_2O_7$,	.02053	.01854
Percentage of P in yellow precipitate,	1.603	1.623
Weight of P calculated from yellow precipitate, assuming factor 1.63 per cent.	.02087	.01863

ON THE DETERMINATION OF DIASTATIC ACTION.

By J. R. Duggan.

The various processes in which starch is converted into sugar by the action of disastase make it necessary to have some accurate method by which the converting power of any substance containing this ferment may be determined. Many of the results that have hitherto been published have undoubtedly been obtained

in such a manner that they are not even approximately correct. This has probably been due, not so much to the method employed, as to a disregard of the influence of very minute quantities of various substances, and consequently to a lack of care in the selection of pure reagents.

As diastase cannot be entirely separated from other substances, it is impossible to determine the actual amount present, but the comparative amount may be found by ascertaining the quantity of starch converted into sugar under known conditions.

This power of conversion is known as the "diastatic value" of any substance. The principal conditions affecting the extent of conversion are time, temperature, and the presence of various foreign substances, such as acids, alkalis, etc. The influence exerted by these has already been investigated to some extent by Kjeldahl[1] and others. It has also been shown by Bert[2] that pressure does not influence this reaction.

The method usually adopted for measuring the extent of conversion has been to determine the amount of sugar formed; but some have preferred—probably because it involves less labor—to determine the time required for the conversion into dextrin and sugar of a given weight of starch—using iodine as an indicator. This method is inaccurate, for the following reasons. The rate of conversion, as will be seen later, is not quite proportionate to the time of action; but even if this were true, it is not practicable by means of iodine to fix the time of the disappearance of the starch. This is due to the fact that the dextrin present gives a color with iodine, and there is no time during the reaction at which the blue color suddenly fails to appear when iodine is added, but the blue gradually shades into a purple, and this into a rose color, the intensity of these depending upon the amount of iodine added, as well as on the extent of conversion.

Except when otherwise stated, the following details have been observed in making the determinations described in this paper. The starch paste was made by adding 6 grams of air-dried arrowroot (= 5.420 grams dried at 110°) to 200 cc. of distilled water, and heating the mixture in a water-bath until the starch was thoroughly gelatinised. The flask containing this was then placed in a large water-bath, which was kept at a constant temperature;

[1] Ding. Polytech. J. **235**, 379 and 452; also Centralblatt **11**, 73.
[2] Compt. Rend. **80**, 1579.

and when the starch paste had acquired the temperature of the surrounding water, the requisite quantity of a solution of malt extract was added, and the solutions well mixed by shaking. When it became necessary to stop the reaction, 2 cc. of a 10 per cent. solution of caustic soda were added. The whole was then diluted to a given volume, and the sugar determined as maltose, volumetrically, by Fehling's solution. The errors of this method were found to be too slight to affect the value of results, while the somewhat more accurate method of weighing the precipitated copper oxide was not practicable, in view of the large number of determinations to be made. Arrow-root was used on account of its freedom from alkali, which is usually present in starches made from corn or potatoes. This is due to the use of caustic soda in their extraction and incomplete washing afterwards. In fact it is difficult even by a long washing to remove all the alkali present, and it is probable that a small amount is absorbed and held in combination by the granules, as has been shown to be the case with cellulose.[1] The following table shows the amount of sugar formed from several samples of starch:

No.	Maltose.	No.	Maltose.
1	0.098 gram.	4	0.475 gram.
2	0.328	5	1.423
3	0.135	6	2.010

5 cc. malt solution. Time, 30 minutes. Temperature, 55°.

The first four of these were ordinary laundry starches of different manufacture, the fifth was a corn starch for culinary purposes, and the sixth was arrow-root. Four other samples of arrow-root were examined, and they all gave results agreeing very closely with this one, so it seems that this starch is sufficiently uniform for general use in diastatic determinations.

Distilled water must also be used in making the starch paste and the malt solution. The substitution of hydrant water from the city water supply was found to diminish the conversion by about 40 per cent., this not being quite constant. A sample of rain water was also found to retard the action of the diastase to the extent of 11 per cent. From these facts it will be seen how great care must be exercised to obtain pure reagents. The use of water redistilled

[1] Mills. J. Chem. Soc. **43**, 142.

from potassium permanganate was found to be unnecessary, as it made no appreciable difference in results.

The malt solution used was a 5 per cent. solution of a commercial extract. A minute quantity of free acetic and lactic acids present (amounting usually to about 0.01 gram NaOH to 100 cc.) was carefully neutralised with caustic soda. In making analyses for commercial purposes this precaution is scarcely necessary, for when the usual quantity of malt solution is added to the starch paste, the dilution is so great that the very minute quantity of acid present could cause only a very slight error. The solution under examination should, however, always be examined, for there might be present a much larger amount of free acid, especially if fermentation has taken place. In such a case it should, of course, be neutralised.

The Influence of Acids and Alkalis on Diastatic Action.

It has already been seen from the experiments on various starches that diastase is very much retarded in its action by the presence of quite small amounts of alkali. The diminished conversion when ordinary water is used seems to be due to slight alkalinity also. The following table shows the effect of very minute quantities of caustic soda:

Parts of NaOH per 1,000,000 of starch paste.	Maltose.
0	1.992 grams.
10	1.578
15	0.921
20	0.520

Malt solution, 5 cc. Time, 30 minutes. Temperature, 55°.

There is very little or no conversion when somewhat greater quantities of alkali are used. The proportion of caustic soda to the starch in these experiments was respectively 0.033, 0.050 and 0.066 of one per cent. The effect of carbonates and other alkaline salts I have not yet investigated.

My experiments on the influence of acids have led me to doubt the general statement that diastase acts best in a slightly acid medium; or, if this is true, the amount of acid required for this is certainly very much more minute than is usually stated, as is shown by the following table:

Parts of H_2SO_4 per 1,000,000 of starch paste.	Maltose.
0	2.003 grams.
5	2.035
10	1.913
20	1.053

Malt solution, 2 cc. Time, 1 hour. Temperature, 55°.

There is here an increase in sugar production of only 1.5 per cent. when 0.0005 of one per cent. of sulphuric acid is used, which at first sight seems to be due to the favorable action of the acid on the diastase, but I am inclined to think that this would not take place with perfectly pure starch. The starch used in these experiments, while perfectly neutral, made the reaction of the litmus less sharp, owing, no doubt, to certain salts contained in the granules, and which could not be entirely washed out with water alone. If an acid was added to the wash water it only complicated matters, by remaining itself in combination with the starch. As the amount of acid which increased the conversion was equal to only $\frac{1}{2000}$ of the starch used, it is very possible that this does not remain free, but enters into combination with certain salts naturally present in the starch. This, together with the fact that 0.001 of one per cent. of acid considerably retards the conversion, makes it appear probable that diastase acts as rapidly on pure starch as in an acid solution. I hope, however, to decide this point more definitely, using soluble starch that has been purified by repeated precipitation. Diastase will also be prepared as pure as possible, and used instead of malt extract, which, of course, contains phosphates and other salts that may affect the reaction. A closer study of this point will perhaps be of use in fixing the conditions necessary to obtain a proper and uniform action of diastase in the mash tub. The statement of Jungk[1] that diastase is much more active in a solution containing 0.033 of one per cent. of hydrochloric acid is certainly incorrect, and is probably due to the use of alkaline starch. If this were true, it is not probable that a slight increase of this amount (0.05 of one per cent.) would, as he states, entirely prevent conversion.

Influence of Time on Diastatic Action.

In the first series of experiments on this point a specimen of ordinary starch containing alkali was used, and the rate of sugar

[1] Phar. J. Trans. (3) **14**, 104.

production was found to decrease rapidly as the time advanced; but when neutral starch was used this was not the case. The only explanation of this fact seems to be that the effect of the alkali increases with the time of exposure. When the solution is neutral, the amount of starch converted is almost directly proportional to the time of action, as is shown by the following table:

Time.	Maltose.	Conversion per min.
5 minutes.	0.214 gram.	0.0428 gram.
10	0.416	0.0416
20	0.806	0.0403
40	1.593	0.0398
60	2.033	0.0339

Malt solution, 2 cc. Temperature, 55°.

The decrease in the rate of conversion shown in the last experiment of this series is not due to a lessening of the activity of the diastase, but to the fact that over one-third of the starch had been converted into maltose. As is shown later, the reaction is always retarded under these circumstances. A series of experiments extending over a longer time gave the following results:

Time.	Maltose.	Conversion per min.
1 hour.	2.284 grams.	0.038 gram.
2 hours.	4.301	0.035
2 hours 30 minutes.	5.257	0.035

Malt solution, 2 cc. Temperature, 55°. 500 cc. of 3.5 per cent. starch paste.

The fact that the extent of conversion is not quite proportional to the time of action is probably due, merely, to the gradual dilution of the starch paste, owing to the change which is taking place; and if the starch was replaced as fast as it was converted, there is every reason to suppose that the diastase would continue its action indefinitely. It is not therefore, as Baswitz[1] has claimed, used up in the reaction; and it is probable that the same is true of the other soluble ferments. These results also seem to show that the starch molecule breaks up directly into dextrin and maltose, and not into dextrin first and this into maltose; for if this was the case, in the first part of the time during which the dextrin was forming there should be formed little or no maltose, while later the production of maltose should become more rapid.

[1] Berichte **11**, 1443.

The Influence of the Amount of Diastase on the Rate of Conversion.

The statement of Baswitz[1] that with a given amount of starch the conversion was not proportional to the amount of diastase, has been shown by Kjeldahl[2] to be incorrect, provided the quantity of maltose formed is not greater than 45 per cent. of the starch used. The results obtained by Kjeldahl do not, however, show very close agreement, since he found that on using three times the quantity of malt solution, the proportionate extent of conversion was diminished by from 10 to 17 per cent.

The action seems to be slightly diminished when the amount of diastase is increased; but this, within ordinary limits, amounts to a very small percentage. The starch converted into maltose should not exceed 35 per cent. of the whole amount, and it is better that it should not be less than 5 per cent., as in this case the large quantity of starch left in solution interferes with the precipitation of the copper oxide. The extent of conversion produced by varying amounts of malt solution is shown in the following series of experiments:

Malt Solution.	Maltose.	Conversion per cc.
1 cc.	0.475 gram.	0.475 gram.
2	0.937	0.469
3	1.381	0.460
5	2.269	0.454
7	2.790	0.399
10	3.196	0.320

Time, 30 minutes. Temperature, 55°.

The effect of a too small excess of starch is shown in the last two of these experiments.

The temperature of 55° C. is best suited for diastatic determinations, for not only does the greatest action take place at about this degree, but any accidental variation of two or three degrees either above or below 55° will make no appreciable difference in the amount of sugar formed. The experiments given in this paper have all been performed at this temperature, but a sufficient number have been made at other temperatures to show that the facts established are not confined to any temperature at which there is action, provided it is not so high as to injure the diastase.

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[1] Berichte **12**, 1827. [2] Ding. Polytech. J. **235**, 379.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

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(Continued from p. 238.)

ARSENOSO-TUNGSTATES.

The alkaline salts belonging to this series are easily prepared by boiling arsenous oxide with strong solutions of acid tungstates, as, for example, with 12 : 5 or 10 : 4 sodic salt. The arsenous oxide should be in excess to secure complete saturation. The filtered solution on standing usually deposits crystals of arsenous oxide in greater or less quantity. The salts of this series are either colorless or pale yellow. They are not very easily oxidised in acid solutions, but in presence of an excess of alkali they absorb oxygen from the air and are converted into arsenio-tungstates. Bromine and chlorine readily oxidise such solutions. The arsenoso-tungstates are, as a rule, more soluble than arsenio-tungstates. They are very stable and well defined, and may as a class be embraced under the general formula

$$m\mathrm{WO_3}.n\mathrm{As_2O_3}.p\mathrm{R_2O},$$

in which n is usually greater than unity.

Analytical Methods.—Hydric sulphide precipitates arsenous sulphide from these salts, and usually without sensible reduction of the tungstic teroxide. It is best to precipitate from a hot solution, and to pass the current of the gas for a long time to insure complete decomposition. The arsenous sulphide may then be collected and weighed upon a Gooch asbestos filter. The tungstic oxide may be determined in the filtrate by mercurous nitrate in the usual manner. The simplest and most satisfactory method of determining the arsenic is by titration with iodine in a solution containing an excess of sodic or potassic bicarbonate. Finally, it is possible to determine the arsenic by oxidising the solution with bromine after adding an excess of an alkaline carbonate, and then precipitating the arsenic in the form of ammonio-magnesic arsenate. The precipitate must be redissolved in dilute chlorhydric acid and precipitated a second time.

The alkaline arsenoso-tungstates are, as a rule, easily soluble; the crystalline salts are often soft and gummy, though well defined.

They appear in some cases to be decomposed more or less completely by solution and evaporation, with separation of arsenous oxide and formation of new salts of different series. In certain cases the addition of a salt of one of the heavy metals determines the precipitation of crystals of arsenous oxide in quantity. It is well known that alkaline hydrates also dissolve arsenous oxide in a proportion more than sufficient to form definite salts, and that the solutions deposit crystals of arsenous oxide on standing.

9 : 1 *Ammonic Arsenoso-tungstate.*—A boiling strong solution of 12 : 5 sodic tungstate dissolves arsenous oxide very readily, and in large quantity. The solution on evaporation gives a colorless or very pale yellow thick gummy mass, which on re-solution leaves octahedral crystals of arsenous oxide. The solution of the sodic salt gives with ammonic chloride, after standing some time, beautiful pale yellow almost colorless prisms. These may be re-dissolved and recrystallised without decomposition. Of this salt,

1.2699 gram lost on ignition 0.2750 gram = 21.65 per cent. H_2O, As_2O_3, and NH_3.

1.3508 gram gave by titration with iodine 0.1034 gram As_2O_3 = 7.65 per cent.

1.9457 gram gave 0.2713 gram NH_4Cl = 6.78 per cent. $(NH_4)_2O$.

0.9776 gram gave 0.7732 gram WO_3 = 79.09 per cent. by $Hg_2(NO_3)_2$ and ignition.

The analyses lead to the formula

$$18WO_3.2As_2O_3.7(NH_4)_2O + 18Aq,$$

which requires:

		Calculated.	Found.
$18WO_3$	4176	79.39	79.09
$2As_2O_3$	396	7.53	7.65
$7(NH_4)_2O$	364	6.92	6.78
$18H_2O$	324	6.16	6.48
	5260	100.00	

The salt may of course be regarded as a double salt, but in this class of salts, as in the arsenio-tungstates and phospho-tungstates, I am disposed to think that in all cases we have an even number of molecules of tungstic oxide united with at least *two* molecules of arsenous oxide. Further investigations are of course required to settle this question. Meantime, from the analogy of the baric salt, we may write the formula provisionally as

$$9WO_3.As_2O_3.4(NH_4)_2O + 9WO_3.As_2O_3.3(NH_4)_2O + 18Aq.$$

9:1 *Baric Arsenoso-tungstate.*—A solution of sodic arsenoso-tungstate obtained as above gives a white crystalline precipitate with baric chloride which is nearly insoluble in water, and which was therefore only washed upon the filter and dried on woollen paper for analysis. In this salt,

1.1037 gram ignited with WO_4Na_2 lost 0.1290 gram = 11.69 per cent. H_2O.

1.9764 gram titrated with iodine gave 6.15 per cent., 6.38 per cent., 6.18 per cent. As_2O_3, mean 6.23 per cent.

1.5652 gram gave 0.4358 gram SO_4Ba = 18.28 per cent. BaO.

In determining the arsenous oxide the salt was first dissolved in very dilute chlorhydric acid, an excess of sodic bicarbonate being added before titration. The analyses correspond with the formula

$$9WO_3.As_2O_3.4BaO + 21Aq,$$

which requires:

		Calculated.	Found.
$9WO_3$	2088	63.74	63.80
As_2O_3	198	6.04	6.23
$4BaO$	612	18.68	18.28
$21H_2O$	378	11.54	11.69
	3276	100.00	

The formula may be

$$18WO_3.2As_2O_3.8BaO + 42Aq.$$

I have stated above that arsenoso-tungstates pass readily into arsenio-tungstates by oxidation and assumption of two additional atoms of oxygen. It seemed, therefore, natural to suppose that other simple or complex molecules might also be added to the molecule of arsenous oxide entering into the complex acid. I shall hereafter give the results of a detailed examination of this subject.

16:8 *Sodic Arsenoso-tungstates.*—Arsenous oxide dissolves readily in 10:4 sodic tungstate on boiling. When an excess of arsenic is present, the filtrate, after evaporation to the consistency of a syrup, deposits on spontaneous evaporation large colorless prismatic crystals. These dissolve readily in water without decomposition, and may be recrystallised until perfectly pure. After four recrystallisations,

0.9451 gram gave with CO_3NaH and iodine 0.2178 gram As_2O_3 = 23.05 per cent.

0.6128 gram gave with CO_3NaH and iodine 0.1416 gram As_2O_3 = 23.10 per cent.

1.1327 gram gave 0.3237 gram As_2S_3 = 23.01 per cent. As_2O_3.

0.9225 gram gave 0.5005 gram WO_3 = 54.26 per cent.

1.0614 gram gave 0.5781 gram WO_3 = 54.46 per cent.

0.8517 gram gave 0.1238 gram H_2O = 14.54 per cent.

The analyses agree well with the formula

$$16WO_3.8As_2O_3.9Na_2O + 55Aq,$$

which requires:

		Calculated.	Found.		
$16WO_3$	3712	54.23	54.28	54.46	
$8As_2O_3$	1584	23.14	23.05	23.10	23.01
$9Na_2O$	558	8.16		8.04 (diff.)	
$55H_2O$	990	14.47		14.54	
	6844	100.00			

The salt gives off vapors of arsenous oxide even on gentle heating, and the determination of the water cannot be made by the use of sodic tungstate. After many trials, it was found best to mix the salt in a porcelain boat with plumbic oxide and carefully heat in a combustion tube, collecting the water in asbestos drenched with sulphuric acid. This process, suggested by my assistant, Mr. Herman Schmidt, gave good results in this case. A solution of the salt gives white flocky crystalline precipitates with baric, strontic and calcic chlorides. Mercurous nitrate gives a pale yellow precipitate, which becomes darker on heating, and finally takes a dirty greenish-white color. Argentic nitrate gives a milk-white precipitate, which remains suspended for a long time. Manganous sulphate gives no precipitate, but the solution becomes yellow, and after standing some time, yields beautiful bright yellow tabular crystals. Ammonic and potassic arsenates and orthophosphates give white crystalline precipitates, which appear to be respectively arsenoso-arsenio-tungstates and arsenoso-phospho-tungstates. The mother liquor of the 16 : 8 salt gives on evaporation a few crystals in a thick colorless syrup, which, after a few days, forms a pale yellowish hard gummy mass. This may prove to contain a second arsenoso-tungstate. The best method of preparing the beautiful 16 : 8 salt in quantity will probably be to mix 12 : 5 or 10 : 4 sodic tungstate and arsenous oxide in the precise ratio indicated by the formula of the salt,

and, after adding water, to boil until the arsenous oxide is dissolved.

ARSENOSO-MOLYBDATES.

Arsenoso-molybdates are formed under the same conditions as arsenoso-tungstates, by boiling solutions of acid molybdates with an excess of arsenous oxide. In this case also there is always a sort of supersaturation, and arsenous oxide separates from the solution on cooling. The general statements made concerning the arsenoso-tungstates apply to these salts also. The general formula is

$$m\mathrm{MoO_3}.n\mathrm{As_2O_3}.p\mathrm{R_2O},$$

in which n is usually greater than unity. The salts are often beautifully crystalline.

Analytical Methods.—Arsenous oxide may be determined in these salts by oxidising the solutions in presence of an excess of an alkaline carbonate by means of bromine, and precipitating as ammonio-magnesic arsenate. The precipitation must be repeated a second time, but the final treatment with ammonic sulphide, which I have recommended for the separation of phosphoric and molybdic oxides, is of course inadmissible. By far the best method of determining the arsenic in these salts is titration with iodine after addition of an excess of an alkaline bicarbonate. It is not possible to determine the oxides of molybdenum and arsenic together by precipitation with mercurous nitrate, since no amount of care suffices to prevent the volatilisation of arsenic in the subsequent ignition. For the same reason, it is also very difficult to determine the water of crystallisation by the ignition loss, as fumes of arsenous oxide are given off at temperatures which are much below that at which sodic tungstate fuses. The degree of facility with which this takes place varies with the salt to be analysed. As regards the determination of the water, I have found it best to heat gently in a porcelain crucible, supported over a small iron cup heated from below, but even in this case the results are never very satisfactory. Arsenous oxide cannot be separated from molybdic oxide by hydric sulphide, since molybdic sulphide is always precipitated at the same time, even when phosphoric acid has been added in excess. I have, however, found that fairly good determinations of molybdic oxide may be made in many cases by dissolving, boiling with a small excess of ammonia, adding a little ammonic chloride, and finally precipitating with baric chloride. The baric molybdate

may then be ignited and weighed upon an asbestos filter. The results, if not very accurate, are at least sufficiently close to be of great service as verifications of formulas.

8 : 2 *Baric Arsenoso-molybdate.*—A boiling strong solution of 14 : 6 ammonic molybdate dissolves arsenous oxide in large quantity, and very readily. The solution has usually a yellowish-green color from slight reduction of the molybdic teroxide. After filtration and evaporation upon a water-bath, it deposits an abundance of octahedral crystals of arsenous oxide. The filtrate from these does not yield crystals on standing, but after evaporation upon the water-bath solidifies to a greenish gummy mass, readily soluble in water, often, however, leaving a residue of arsenous oxide. The solution of this gummy salt gives a white crystalline precipitate with baric chloride. The filtrate from this, after evaporation and standing, yields an abundance of beautiful very pale greenish crystals, which may be redissolved and recrystallised without decomposition. In this salt,

1.1230 gram lost on heating 0.1126 gram = 10.03 per cent.
1.0548 gram gave 0.3258 gram SO_4Ba = 20.28 per cent. BaO.
0.3919 gram gave 0.0678 gram As_2O_3 = 17.31 per cent.
0.5774 gram gave 0.0995 gram As_2O_3 = 17.23 per cent.
0.9729 gram gave 1.0383 gram MoO_4Ba = 51.74 per cent. MoO_3.

The analyses lead to the formula

$$8MoO_3.2As_2O_3.3BaO + 13Aq,$$

which requires:

		Calculated.		Found.		
$8MoO_3$	1152	51.41	69.08	51.74		69.01
$2As_2O_3$	396	17.67		17.31	17.23	
$3BaO$	459	20.48		20.28		
$13H_2O$	234	10.44		10.03		
	2241	100.00		99.32		

The arsenous oxide was determined in the first analysis by boiling with a solution of sodic dicarbonate, filtering, and titrating with iodine; in the second, by direct titration without previous filtration. The baryta was separated by fusion with sodic carbonate, and weighed as sulphate. The water was found by heating over a radiator until a constant weight was obtained, as it was impossible to ignite with sodic tungstate without volatilisation of arsenous oxide.

The salt requires a very large quantity of water for solution. The dry salt in fine powder boiled with argentic nitrate gives a beautiful yellow crystalline salt. Thallous nitrate yields, under the same circumstances, a very pale yellow, also crystalline salt. The mercurous salt is pale yellow, but not distinctly crystalline.

12:5 *Arsenoso-molybdate of Ammonium.*—When a solution of zincous sulphate is added to one of the gummy arsenoso-molybdate of ammonium, no precipitate is found at first, but after a time colorless crystals are formed which do not contain zinc, and which may be recrystallised without apparent decomposition. The salt dissolves in a large quantity of water to a colorless solution. It is only partially decomposed by boiling with mercurous nitrate. In this compound,

0.7105 gram gave 0.0326 gram $(NH_4)_2O$ = 4.58 per cent.
0.9785 gram gave 0.0455 gram $(NH_4)_2O$ = 4.65 per cent.
1.2612 gram gave 1.3720 gram MoO_4Ba = 52.74 per cent. MoO_3.
1.3081 gram gave 0.3856 gram As_2O_3 = 29.48 per cent.
0.6044 gram gave 0.1787 gram As_2O_3 = 29.55 per cent.

The analyses correspond fairly well with the formula

$$12MoO_3.5As_2O_3.3(NH_4)_2O + 24Aq,$$

which requires:

		Calculated.		Found.		
$12MoO_3$	1728	52.28 } 82.21		52.74		} 82.24
$5As_2O_3$	990	29.94 }		29.48	29.55	
$3(NH_4)_2O$	156	4.71		4.58	4.65	
$24H_2O$	432	13.07		13.15		
	3306	100.00				

The reactions of this salt were studied by acting with metallic solutions upon the finely pulverised substance, so as to avoid, if possible, the decomposing action of water. In this manner cold solutions of argentic and thallous nitrates give beautiful colorless granular crystals. Baric chloride gives a white colorless salt more flocky than the ammonium compound. Manganous sulphate does not react in the cold, but on boiling for some time, a beautiful pale canary-yellow crystalline salt is formed. Cupric sulphate does not act when cold, but on boiling a clear solution results.

6:3 *Arsenoso-molybdate of Manganese.*—A portion of the dry gummy mass of arsenoso-molybdate of ammonium, which had stood for some time in the laboratory, was redissolved and filtered

from a small quantity of arsenous oxide. The filtrate gave no precipitate with manganous sulphate, but, on boiling, the fine green solution became much lighter in color, then turbid, and finally deposited very beautiful bright orange-colored octahedral crystals insoluble in water. Of this salt,

0.5961 gram gave 0.2052 gram $As_2O_3 = 34.41$ per cent.

0.7341 gram gave 0.1216 gram $P_2O_7Mn_2 = 8.28$ per cent. MnO.

0.6362 gram lost on heating over a radiator 0.0428 gram = 6.73 per cent.

The analyses correspond to the formula

$$6MoO_3.3As_2O_3.2MnO + 6Aq,$$

which requires:

		Calculated.	Found.
$6MoO_3$	864	50.59	50.58
$3As_2O_3$	594	34.78	34.41
$2MnO$	142	8.31	8.28
$6H_2O$	108	6.32	6.73
	1708	100.00	

The molybdic oxide was determined by difference only. By mixing a solution of the gummy arsenoso-molybdate of ammonium with solutions of zincous and cupric sulphates respectively, after standing, beautiful octahedral crystals were deposited, which in the case of the zinc salt were colorless, in that of copper, of a fine green. The corresponding nickel salt was also in beautiful green octahedral crystals. In the zinc salt,

0.2378 gram gave 34.52 per cent. As_2O_3 by titration with iodine.

0.3115 gram gave 34.47 per cent. As_2O_3 by titration with iodine.

0.2169 gram gave 34.56 per cent. As_2O_3 by titration with iodine.

The formula

$$6MoO_3.3As_2O_3.2ZnO + 6Aq$$

requires 34.38 per cent. In the copper salt,

0.2619 gram gave 34.67 per cent. As_2O_3 by titration with iodine.

0.2006 gram gave 34.89 per cent. As_2O_3 by titration with iodine.

The formula

$$6MoO_3.3As_2O_3.2CuO + 6Aq$$

requires 34.41 per cent.

In the cases of both the zinc and copper salts a trace of free arsenous oxide was probably mixed with the salt analysed. The

nickel salt doubtless corresponds to the other three. In the case of the manganese salt, fumes of arsenous oxide were given off at very low temperatures. The pale canary-yellow manganese salt obtained by precipitating the 12 : 5 ammonic salts with manganous sulphate corresponded to the formula

$$6MoO_3.3As_2O_3.2MnO + 15Aq.$$

0.1727 gram gave 31.77, 31.62 and 31.73 per cent. As_2O_3 by titration with iodine.

1.1393 gram gave 0.0898 gram Mn_3O_4 = 7.33 per cent. MnO.

The formula given requires 31.77 per cent. As_2O_3 and 7.59 per cent. MnO. The salt gave off arsenous oxide very freely when heated with sodic tungstate.

PHOSPHOROSO-TUNGSTATES.

I have already described the class of phosphoroso-molybdates, and will now consider the parallel group of phosphoroso-tungstates. The alkaline salts of this series are readily formed by the action of phosphorous and chlorhydric acids upon metatungstates of the higher order. They are, as a rule, better defined than the corresponding phosphoroso-molybdates, and are in all probability very numerous. The compounds to be described will be sufficient to open the subject for further investigation. The analytical methods employed were the same as in the case of the corresponding molybdenum salts, except that after oxidation of phosphorous to phosphoric acid, tungsten and phosphorus were usually precipitated together by mercurous nitrate and mercuric oxide.

22 : 4 : 6 *Ammonic Phosphoroso-tungstate.*—When the solution of phosphorous and chlorhydric acids formed by the action of water upon phosphoric terchloride is poured upon crystalline 12 : 5 ammonic tungstate, the salt packs at once into a dense mass. This is to be well rubbed up in a mortar with a large excess of the acid liquid, and allowed to stand for twenty-four hours. The greater part of the mass then presents large granular colorless crystals. A much smaller proportion of a white fine-grained salt is formed at the same time, and is easily separated by washing from the heavier crystals of the granular salt. This last may be washed with cold water on the filter pump, and dried on woollen paper. In mass the crystals present a faint but distinct tinge of yellow. The salt is but slightly soluble in cold water, but dissolves

in a rather large proportion of boiling water to a yellow liquid. The solution gives no precipitate with cupric sulphate, but the mixed liquid becomes somewhat darker on boiling. With argentic nitrate it gives a turbid solution, which becomes purplish on heating, and finally gives a dark dull-purple precipitate. With mercurous nitrate the solution gives a white light precipitate, which becomes deep yellow on heating, and regains its white color on cooling. In this salt,

1.6407 gram gave 0.1136 gram $P_2O_7Mg_2$ = 5.12 per cent. PO_3H_3.

1.7666 gram gave 0.1256 gram $P_2O_7Mg_2$ = 5.26 per cent. PO_3H_3.

1.5933 gram gave 0.0791 gram $(NH_4)_2O$ = 4.96 per cent.

1.7340 gram lost with WO_4Na_2 0.2253 gram = 12.99 per cent.

The analysis is of course subject to the corrections indicated by the equation

$$2PO_3H_3 = P_2O_5 + OH_2 + 4H.$$

The results agree very well with the formula

$$22WO_3.4PO_3H_3.6Am_2O + 25Aq,$$

or

$$22WO_3.4[H.PO.2OH]\,6(NH_4)_2O + 25Aq,$$

which requires:

		Calculated.	Found.	
$22WO_3$	5104	82.40	82.46	
$4PO_3H_3$	328	5.29	5.26	5.12
$6(NH_4)_2O$	312	5.04	4.96	
$25H_2O$	450	7.27	7.32	
	6194	100.00		

The phosphorous acid was oxidised by bromine after adding an excess of sodic carbonate. The salt is quietly decomposed by heating, giving a mixture of $WO_3.W_2O_5$ and P_2O_5.

32:16:5 *Potassic Phosphoroso-tungstate.*—This salt was formed, like the ammonium salt, by the action of a mixture of phosphorous and chlorhydric acids upon crystallised 10:4 potassic tungstate. In this case also, two salts appear to be formed—a heavier colorless crystalline salt in relatively large quantity, and a lighter fine-grained salt easily removed by careful washing. Of these only the first was examined. Of this salt,

1.4225 gram gave 1.2124 gram oxides = 85.23 per cent. $WO_3 + P_2O_5$.

1.3877 gram gave 0.2428 gram $P_2O_7Mg_2$ = 11.19 per cent. P_2O_5 = 12.96 per cent. PO_3H_3.

1.3949 gram lost 0.1406 gram = 10.08 per cent.

The analyses correspond to the formula

$$32WO_3.16PO_3H_3.5R_2O + 46Aq,$$

or

$$32WO_3.16[H.PO.2OH]5R_2O + 46Aq,$$

which requires:

		Calculated.	Found.
$32WO_3$	7424	73.97	74.04
$16PO_3H_3$	1312	13.07	12.96
$5R_2O$	472	4.70	4.69 (diff.)
$46H_2O$	828	8.26	8.31
	10036	100.00	

The salt is but slightly soluble even in boiling water. It has no yellow tint.

22:8:2 *Sodic Phosphoroso-tungstate.*—This salt was formed, like the last, by the action of a mixture of phosphorous and chlorhydric acids upon crystallised 10:4 sodic tungstate. The action is very energetic. The colorless crystals of the tungstate soon disappear, and are replaced by yellow granular crystals in large quantity. The yellow crystals were well washed upon the filter-pump with cold water, and dried on woollen paper. Of this salt,

1.7082 gram gave 1.4895 gram oxides = 87.19 per cent. $WO_3 + P_2O_5$.

1.3623 gram gave 0.1870 gram $P_2O_7Mg_2$ = 8.78 per cent. P_2O_5 = 10.15 per cent. PO_3H_3.

1.3532 gram lost with WO_4Na_2 0.1481 gram = 10.94 per cent.

The analyses correspond to the formula

$$22WO_3.8PO_3H_3.2Na_2O + 35Aq,$$

which requires:

		Calculated.	Found.
$22WO_3$	5104	78.36	78.40
$8PO_3H_3$	656	10.07	10.15
$2Na_2O$	124	1.90	1.87 (diff.)
$25H_2O$	630	9.67	9.58
	6514	100.00	

The sodium salt is nearly insoluble in cold water, and but slightly soluble in boiling water. The undissolved portion takes a much brighter yellow color. As in the cases of the potassium and ammonium salts, a small quantity of a second salt, in very small crystals and of a white color, is formed at the same time.

PHOSPHOROSO-MOLYBDATES (*again*).

As the phosphoroso-molybdate of ammonium, which I have described in another part of this paper, appeared to contain a trace of phosphoric acid, I repeated the preparation with a perfectly pure solution of phosphorous acid obtained by the action of water upon phosphorous chloride. The liquid contained, of course, free chlorhydric acid, and was poured into a cold strong solution of 14:6 ammonic molybdate. A sulphur-yellow precipitate was at once formed, consisting of very minute talcose scales. The salt was washed on the filter-pump very thoroughly with cold water, and dried on woollen paper. It is readily soluble in hot water to a yellow liquid. The solution on boiling reduces mercuric chloride to mercurous chloride. It gives an abundant white, flocky precipitate with argentic nitrate, which on long boiling becomes darker. Finally, silver is reduced. In this preparation,

0.7247 gram lost with WO_4Na_2 0.1150 gram = 15.87 per cent.

0.8323 gram gave 0.0386 gram $(NH_4)_2O$ = 4.64 per cent.

0.7426 gram gave 0.0776 gram $P_2O_7Mg_2$ = 6.68 per cent. P_2O_5.

0.9517 gram gave 0.0994 gram $P_2O_7Mg_2$ = 6.68 per cent. P_2O_5.

The phosphorous acid was oxidised by bromine in presence of an excess of CO_2NaH. The analyses correspond most nearly to the formula

$$24MoO_3.4PO_3H_3.4(NH_4)_2O + 25Aq,$$

which requires:

		Calculated.		Found.	
$24MoO_3$	3456	77.80 } 85.18		77.45 } 85.16	
$4PO_3H_3$	328	7.38 }		7.71 }	
$4(NH_4)_2O$	208	4.68 } 14.82		4.64 } 14.84	
$25H_2O$	450	10.14 }		10.20 }	
	4442	100.00			

The analyses confirm the formula first obtained, though the new salt contains eight molecules more of water of crystallisation.

ANTIMONOSO-TUNGSTATES.

When solutions of an acid tungstate of sodium are boiled with antimonious oxide, the latter very slowly dissolves, and it is difficult to obtain perfectly saturated solutions. It is best to employ antimonious oxide which has been freshly precipitated from the corresponding chloride by sodic carbonate and washed by decantation with cold water. If the precipitated oxide is allowed to stand for some time it becomes crystalline, and is then no longer available. The solution of antimonoso-tungstate obtained in this manner has a yellow color, and there is no sensible reduction of tungstic teroxide. Instead of this process the following may be employed with advantage. Freshly precipitated antimonious oxychloride, SbOCl, after washing with cold water, dissolves very readily in boiling solutions of alkaline tungstates of the metatungstic series. The solutions obtained in this way are also yellow. The oxychloride, on standing for some days, also becomes highly crystalline, and then dissolves with great difficulty. The solutions of sodic salts obtained as above become on evaporation thick and syrupy, and finally yield yellow gummy masses. There is in these cases also a tendency to supersaturation, as with the arsenoso-tungstates, though by no means to the same extent, and crystals of antimonious oxide (hydrate?) are sometimes deposited. The concentrated solution of the sodic salt obtained as above gives yellow oils with strong solutions of potassic or ammonic salts, which are but slightly soluble in a large excess of the latter. After pouring off the supernatant liquid, the oils may be redissolved in a small quantity of water, and again precipitated by a large excess of a concentrated solution of a potassic salt. I prefer for this purpose the bromide. Two or three repetitions of this process yield a nearly pure potassic antimonoso-tungstate, which may be advantageously used in the preparation of other salts. The alkaline salts of this series are either oily liquids or gummy masses with a pale yellow color, and very easily soluble. The solutions absorb oxygen rather slowly from the air, and are not easily oxidised by bromine or chlorine, unless in presence of an excess of alkali, as, for example, sodic bicarbonate. They then pass into antimonio-tungstates. The general formula of the antimonoso-tungstates is

$$m\mathrm{WO_3}.n\mathrm{Sb_2O_3}.p\mathrm{R_2O}.$$

Analytical Methods.—The quantitative separation of antimony from tungsten in these compounds may be effected by the following methods. Hydric sulphide passed through the solution previously acidulated with chlorhydric acid precipitates antimonious sulphide completely, without any sensible reduction or precipitation of tungsten. An aliquot portion of the sulphide may then be heated in an atmosphere of dry carbonic dioxide, in the usual manner. This method applies to the greater number of cases. In its place we may often, but not always, employ the following, which usually gives good results in the cases of the alkaline salts. Potassic cyanide, as free as possible from carbonate and cyanate, is to be fused in a crucible of Berlin porcelain, and then allowed to cool. A weighed portion of the antimonoso-tungstate is then to be placed upon the fused mass, and the whole cautiously heated to low redness, and kept for a short time at this temperature. The antimony is completely reduced to metal, and after the solution of the alkaline salts in cold water, and washing at first with water and afterward with alcohol, may be weighed upon an asbestos filter. It will be seen that this process is the same as that devised many years ago by myself for the separation of tin from tungsten, worked out in my laboratory by Mr. F. H. Talbutt,[1] and known as Talbutt's method. The process unfortunately does not apply to cases in which insoluble compounds are formed together with the reduced metallic antimony. As a rule, when the process is successful, the antimony is finally in the form of large bright metallic globules, but in some cases it forms on reduction wholly or partially a black powder containing tungsten, and the method then fails. In these cases an accurate result may be obtained by mixing the salt or the potassic cyanide with a quantity of potassic or sodic carbonate sufficient to completely saturate both the tungstic and antimonic oxides present. This variation in the application of the method is due to my assistant, Mr. Herman Schmidt. In determining antimonious or antimonic oxides by this process, there is, of course, the disadvantage that a higher is always estimated from a lower molecular weight. The following analyses will serve to show the degree of accuracy which may be obtained under favorable circumstances, the method applying to antimonio-tungstates as well as to the antimonoso series. In an antimonio-tungstate of potassium not of definite constitution,

[1] Am. Journal of Science and Arts **50**, 7.

1.0924 gram gave 0.4407 gram metallic antimony = 53.79 per cent. Sb_2O_5.

1.0316 gram gave 0.4155 gram metallic antimony = 53.71 per cent. Sb_2O_5.

In another compound,

0.9059 gram gave 0.2251 gram metallic antimony = 33.13 per cent. Sb_2O_5.

1.0312 gram gave 0.2558 gram metallic antimony = 33.08 per cent. Sb_2O_5.

Antimonious oxide may also be determined in these compounds by titration with iodine, after adding to the solution an alkaline tartrate and an excess of sodic bicarbonate. It will be found advantageous to standardise the solution of iodine by means of pure crystallised antimonio-potassic tartrate—of course, after addition of an alkaline dicarbonate.

The determination of tungstic oxide may be effected by first separating the antimony as sulphide, and then precipitating the hot solution with baric chloride, after adding ammonia in small excess. The baric tungstate may be weighed upon an asbestos filter. It is better, however, to precipitate the tungstic oxide by means of mercurous nitrate; only, in case this method is to be applied, the antimony must be precipitated as sulphide after the addition of dilute sulphuric acid, and chlorhydric acid must not be employed.

11 : 3 *Baric Antimonoso-tungstate.*—A solution of sodic antimonoso-tungstate, obtained as above, gives with baric chloride a heavy pale yellow curdy or indistinctly crystalline precipitate. This salt melts under hot water to a thick yellow oily liquid, which dissolves very slowly, requiring a large quantity of water for solution. The solution has a yellow color and an acid reaction. It gives pale yellow flocky precipitates, with mercurous, argentic and thallous nitrates. Of this salt,

1.0722 gram lost on ignition with WO_4Na_2 0.0858 gram = 8.00 per cent.

1.3057 gram gave 0.3318 gram Sb_2S_3 = 21.78 per cent. Sb_2O_3.

1.3668 gram gave 0.3371 gram Sb_2S_3 = 21.17 per cent. Sb_2O_3.

1.2543 gram gave 0.1440 gram SO_4Ba = 7.54 per cent. BaO.

1.4895 gram gave 0.1709 gram SO_4Ba = 7.53 per cent. BaO.

1.9450 gram gave 1.6599 gram oxides ($WO_3 + Sb_2O_4$) = 85.34 per cent.

The analyses lead to the formula

$$11WO_3.3Sb_2O_3.2BaO + 18Aq,$$

which requires:

		Calculated.		Found.		
$11WO_4$	2552	63.07	84.42	62.79	62.99	(diff.) 84.37
$3Sb_2O_3$	864	21.35		21.17	21.78	
2BaO	306	7.57		7.54	7.53	
$18H_2O$	324	8.00		8.00		
	4046	100.00				

The salt may be reduced to the type

$$6WO_3.Sb_2O_3.BaO + 9Aq,$$

if we suppose Sb_2O_3 partially to replace WO_3; but in view of the very frequent recurrence of 22 molecules of tungstic oxide among complex inorganic acids, I am disposed to double the formula given above, and to write

$$22WO_3.6Sb_2O_3.4BaO + 36Aq.$$

In the yellow oily salt obtained by precipitating sodic antimonoso-tungstate by means of potassic bromide, and carefully washing with a cold strong solution of the bromide, the ratio of the tungstic to the antimonious oxide was determined and found to be nearly $8WO_3$ to $2Sb_2O_3$, so that there is probably a series of antimonoso-tungstates with the general formula

$$8WO_3.2Sb_2O_3.nR_2O.$$

The quantity of solution taken gave 0.1091 gram $Sb_2S_3 = 0.0935$ gram Sb_2O_3, and 0.3417 gram $WO_3 = 71.51$ per cent. WO_3 and 21.49 per cent. Sb_2O_3.

ANTIMONOSO-MOLYBDATES.

The salts of this series are readily formed by boiling antimonious oxychloride, SbOCl, with an acid molybdate. The conditions are exactly the same as in the case of the corresponding antimonoso-tungstates. There is almost always a greater or less reduction of the molybdic oxide, and the solutions obtained have a greenish or greenish-blue tint, from the presence of Mo_2O_5 or a similar oxide. The ordinary acid ammonic molybdate of commerce in cold solution readily dissolves freshly precipitated antimonious oxide with only a slight reduction of the molybdic oxide; on boiling, much reduction takes place.

Analytical Methods.—Antimonious oxide cannot be separated from molybdic oxide by means of hydric sulphide, as a greater or less proportion of molybdic sulphide is always found. By proceeding in the manner already pointed out for the separation of antimony from tungsten, it is possible, in many cases at least, to separate antimony from molybdenum with a very satisfactory degree of accuracy. It will be found, however, always advantageous to add a quantity of potassic or sodic carbonate sufficient to neutralise both the molybdic and antimonious oxides before fusion with potassic cyanide. Crucibles of the best Berlin porcelain are alone adapted to fusions of this kind, and even when these are employed the action of the alkaline mixture upon the crucible must be taken into account. The best method is to add to the solution an alkaline tartrate, and then to render it alkaline with an excess of sodic bicarbonate. The antimonious oxide may then be determined by titration with iodine.

17:3 *Ammonic Antimonoso-molybdate.*—This salt crystallises from a solution of antimonious oxide in 14:6 ammonic molybdate, in pale greenish-yellow granular crystals, but its preparation is rather uncertain. It is insoluble in cold water: for analysis, the crystals were simply washed and dried upon woollen paper. In this salt,

0.7474 gram gave by titration with iodine 0.1618 gram Sb_2O_3 = 21.65 per cent.

0.5287 gram gave 0.0399 gram $(NH_4)_2O$ = 7.55 per cent.

1.0869 gram lost on ignition with MoO_4Na_2 and WO_4Na_2 0.1851 gram = 17.03 per cent.

The analyses lead to the formula

$$17MoO_3.3Sb_2O_3.6(NH_4)_2O + 21Aq,$$

which requires:

		Calculated.	Found.
$17MoO_3$	2448	61.18	61.32
$3Sb_2O_3$	864	21.59	21.65
$6(NH_4)_2O$	312	7.79	7.55
$21H_2O$	378	9.44	9.48
	4002	100.00	

The molybdic oxide is estimated by difference. The solution from which this salt of ammonium separated gave, after twenty-

four hours, a fine yellow crystalline precipitate with manganous sulphate. The formula given may be reduced to the type

$$18MoO_3.2Sb_2O_3.6(NH_4)_2O + 21Aq,$$

if we assume that one molecule of Sb_2O_3 plays the part of, or replaces, one molecule of molybdic oxide. In determining the water in this salt I employed a mixture of equal molecules of sodic tungstate and molybdate, which fuses at a temperature below that at which molybdic oxide is given off.

In formulating the arsenoso-tungstates and arsenoso-molybdates I have assumed provisionally that normal arsenites are represented by one or another of the three general formulas

$$As_2O_3.R_2O, \quad As_2O_3.2R_2O, \quad As_2O_3.3R_2O,$$

the three plumbic arsenites forming appropriate special instances. This view would establish a broad line of distinction between arsenites and phosphites, which last are now generally considered as hydryl-phosphinates, the general formula being

$$H.PO.(OH)_2.$$

On the other hand, the existence of alkyl-arsinic acids appears to prove beyond a doubt that at least *some* arsenites belong to the same type with the phosphites. The older view must in any case be true for certain classes of salts, because the arsenites are not all reducible to the type $H.AsO.(OH)_2$, even if we admit that the atom of hydrogen is replaceable by an atom of univalent metal, for which there is no sufficient evidence in the case of the phosphites. If we consider the arsenic in the arsenoso-tungstates and arsenoso-molybdates which I have described to exist in the form of hydryl-arsinic acid, we shall have for the corresponding acids, respectively, the formulas

$$18WO_3 . 4[H.AsO.(OH)_2].8H_2O$$
$$16WO_3 .16[H.AsO.(OH)_2].9H_2O$$
$$8MoO_3. 4[H.AsO.(OH)_2].3H_2O$$
$$12MoO_3.10[H.AsO.(OH)_2].3H_2O$$
$$6MoO_3. 6[H.AsO.(OH)_2].3H_2O$$

in which, of course, the basicity is purely arbitrary, since it depends in each case upon the number of molecules of base in a single salt. The internal basicity, as measured by the hydroxyl in the arsenical term, is always two, corresponding to one in the old style of writing. As the salts described appear to give off all their water when heated,

without other decomposition than loss from the volatilisation of arsenous oxide, it would seem to follow that their formulas must then at least be written as if they contained all the arsenic as As_2O_3, since

$$2[H.AsO.(OH)_2] = As_2O_3 + 3H_2O.$$

PHOSPHOROSO-PHOSPHO-TUNGSTATES.

24 : 1 : 2 : 5 *Potassic Phosphoroso-phospho-tungstate.*—When a solution containing both phosphorous and orthophosphoric acids is added to one of 12 : 5 sodic tungstate, no precipitate is formed, but on adding potassic bromide a white crystalline salt is thrown down, slightly soluble in cold water, but soluble in a large quantity of boiling water, forming a turbid liquid which has an acid reaction. The solution gives no precipitate with cupric sulphate, even on boiling and with or without free chlorhydric acid. It gives a white flocky precipitate with argentic nitrate, which becomes darker on boiling, and finally deep chocolate-brown. This reaction resembles that of the phospho-hypo-phospho-tungstates. The solution gives a very pale yellow indistinctly crystalline precipitate with mercurous nitrate, which is not reduced by boiling, and a white flocky precipitate with baric chloride. The salt dissolves with much difficulty in ammonia-water, but easily in solutions of alkaline carbonates. Chlorhydric acid gives a white precipitate in these solutions, readily soluble in ammonia. In this salt,

1.5373 gram lost on ignition 0.0578 gram = 3.76 per cent.
1.5373 gram gave 1.3702 gram mixed oxides = 89.13 per cent. WO_3 and P_2O_5.

1.7603 gram gave 0.1138 gram $P_2O_7Mg_2$ = 4.13 per cent. P_2O_5.
2.7325 grams gave 0.0836 gram $P_2O_7Mg_2$ = 1.96 per cent. P_2O_5.

In determining PO_3H_3 the solution in CO_3Na_2 was oxidised by bromine.

The analyses correspond with the formula

$$24WO_3.2PO_3H_3.P_2O_5.5K_2O + 13Aq,$$

which requires :

		Calculated.		Found.	
$24WO_3$	5568	84.75	86.91	85.00	86.96
P_2O_5	142	2.16		1.96	
$2PO_3H_3$	164	2.49		2.50	
$5K_2O$	472	7.18		7.11	
$13H_2O$	224	3.41		3.43	
	6570	100.00			

When a solution of phosphorous and chlorhydric acids is mixed with one of the 24 : 1 phospho-tungstate of sodium,

$$24WO_3.P_2O_5.2Na_2O + 27Aq,$$

no precipitate is formed, but after a time relatively large colorless measurable crystals of the phospho-tungstate are deposited.

PHOSPHOROSO-PHOSPHO-MOLYBDATES.

72 : 3 : 2 : 9 *Ammonic Phosphoroso-phospho-molybdate.*—When the solution of phosphorous and chlorhydric acids obtained by treating phosphorous terchloride with cold water is mixed with a solution of 10 : 2 ammonic phospho-molybdate, a greenish-yellow crystalline precipitate is thrown down at once. The salt is very insoluble in water. It was washed upon the filter-pump and dried on woollen paper for analysis. In this salt,

1.0222 gram lost with WO_4Na_2 0.0975 gram = 9.54 per cent.

0.8936 gram gave 0.0354 gram $(NH_4)_2O$ = 3.96 per cent.

1.1348 gram gave 0.0646 gram $P_2O_7Mg_2$ = 3.63 per cent.

1.2439 gram gave 0.0696 gram $P_2O_7Mg_2$ = 3.58 per cent.

The determination of phosphoric oxide was made after oxidation by bromine.

The analyses agree very well with the formula

$$72MoO_3.2PO_3H_3.3P_2O_5.9(NH_4)_2O + 38Aq,$$

which requires :

		Calculated.	Found.
$72MoO_3$	10368	85.61	85.56
$3P_2O_5$	426	3.52	3.58 3.63
$2PO_3H_3$	164	1.35	1.50
$9(NH_4)_2O$	468	3.87	3.96
$38H_2O$	684	5.65	5.58
	12110	100.00	

The formation of this salt may be represented by the equation

$$3[24MoO_3.P_2O_5.3(NH_4)_2O] + 2PO_3H_3 = 72MoO_3.3P_2O_5.2PO_3H_3.9(NH_4)_2O.$$

PHOSPHO-HYPOPHOSPHO-TUNGSTATES.

26 : 4 : 2 *Potassic Phospho-hypophospho-tungstate.*—When the 24 : 1 phospho-tungstate of sodium is boiled with an excess of a solution of hypophosphorous acid and a solution of potassic bromide is added to the clear pale blue filtrate, a white crystalline precipitate is after a time thrown down. The salt dissolves readily in hot water

to a clear solution. This gives a white flocky crystalline precipitate with baric chloride, a pale yellow precipitate with mercurous nitrate, and a white precipitate with argentic nitrate, which on boiling becomes first yellow, then brown, and finally takes a brownish color, and deposits a precipitate closely resembling ferric hydrate. Cuprous sulphate is without action on the solution. For analysis the freshly formed salt was thrown upon a filter, washed on the filter-pump thoroughly with cold water, and finally dried for analysis upon woollen paper. Of this preparation,

1.2162 gram gave 0.9706 gram mixed oxides = 79.81 per cent.
1.9865 gram gave 1.5903 gram mixed oxides = 80.05 per cent.
1.0921 gram gave 0.1408 gram $P_2O_7Mg_2$ = 8.25 per cent. P_2O_5.
1.5059 gram gave 0.1552 gram $P_2O_7Mg_2$ = 6.59 per cent. P_2O_5.
1.2162 gram gave 0.6340 gram $PtCl_6K_2$ = 10.12 per cent. K_2O.
0.9633 gram gave 0.5074 gram $PtCl_6K_2$ = 10.22 per cent. K_2O.
1.2705 gram lost with WO_4Na_2 0.1138 gram = 8.96 per cent.
0.8472 gram lost with WO_4Na_2 0.0778 gram = 9.18 per cent.

In the analyses the hypophosphorous acid was determined by oxidation with bromine, after adding an excess of sodic carbonate. The total phosphoric acid was then determined as ammonio-magnesic phosphate. In another portion of the salt the phosphoric acid proper was precipitated directly by magnesia-mixture in the usual manner. Corrections are of course made for the loss of hydrogen in ignition, according to the equation

$$2PO_2H_3 + H_2O = P_2O_5 + 8H,$$

and also for the retention of one atom of oxygen by the mixed oxides, as shown by the same equation.

The analyses correspond to the formula

$$26WO_3.2PO_2H_3.4P_2O_5.9K_2O.Na_2O + 43Aq,$$

or

$$26WO_3.2[H_2.PO.OH].4P_2O_5.9K_2O.Na_2O + 43Aq,$$

which requires:

		Calculated.	Found.	
$26WO_3$	6032	71.66	71.56	71.80
$4P_2O_5$	568	6.74	6.59	
$2PO_2H_3$	132	1.57	1.55	
$9K_2O$	850	10.09	10.12	10.22
Na_2O	62	0.74	0.78 (diff.)	
$43H_2O$	774	9.20	9.23	
	8418	100.00		

It cannot be doubted that similar compounds containing molybdenum in place of tungsten remain to be discovered. I did not, however, succeed in obtaining them by the action of hypophosphorous acid upon phospho-molybdates, and the precise conditions necessary are yet to be determined. It appears to be at least probable that classes of phosphoroso-hypophospho-tungstates and phosphoroso-hypophospho-molybdates will sooner or later be discovered.

ARSENOSO-PHOSPHO-TUNGSTATES.

The salts of this series are formed when solutions of orthophosphates and arsenoso-tungstates are mixed, and when arsenous oxide is boiled with a solution of an alkaline phospho-tungstate. The alkaline salts are sometimes crystalline and sometimes gummy. The series is probably a very extensive one.

Analytical Methods.—In these salts the arsenous oxide is best determined by titration with iodine after adding an excess of an alkaline dicarbonate. After separating arsenous oxide as sulphide by sulphydric acid, the phosphoric oxide may be determined by magnesia-mixture. Phosphoric and tungstic oxides may be determined together by mercurous nitrate and mercuric oxide after separating arsenous oxide from the solution as arsenous sulphide, dilute sulphuric acid being employed in place of chlorhydric acid. Water is best determined by heating over a radiator.

32 : 14 : 3 : 10 *Potassic Arsenoso-phospho-tungstate.*—This salt was prepared by boiling potassic phospho-tungstate with an excess of finely pulverised arsenous oxide. The filtered solution had a pale greenish-yellow tint, and after standing twenty-four hours deposited a mass of very minute greenish-yellow crystals. These were filtered off, washed with cold water, and then drained by the filter-pump. The drained mass was greenish-yellow, and packed into a gummy solid. The filtrate on evaporation gave a fresh quantity of the same salt, which is rather soluble in cold, and very easily soluble in hot water. Of this salt,

0.9333 gram lost by heating over a radiator 0.0398 gram = 4.27 per cent.

0.9333 gram gave 0.6094 gram $WO_3 + P_2O_5$ = 65.29 per cent.

1.0505 gram gave 0.2413 gram As_2O_3 with iodine = 22.97 per cent.

0.8456 gram gave 0.0472 gram $P_2O_7Mg_2$ = 3.57 per cent.

The analyses correspond fairly well with the formula

$$32WO_3.14As_2O_3.3P_2O_5.10K_2O + 28Aq,$$

which requires:

		Calculated.		Found.	
$32WO_3$	7424	61.51	88.00	61.72	88.26
$14As_2O_3$	2772	22.96		22.97	
$3P_2O_5$	426	3.53		3.57	
$10K_2O$	944	7.82		7.58	
$28H_2O$	504	4.18		4.27	
	12070	100.00			

12 : 2 : 2 : 6 *Sodio-potassic Arsenoso-phospho-tungstate.*—When sodic phospho-tungstate,

$$24WO_3.P_2O_5.2Na_2O + 27Aq,$$

in solution, is boiled with arsenous oxide in excess, this last dissolves freely to a colorless or nearly colorless liquid. On adding ammonic chloride no precipitate is formed, but after acidulating with chlorhydric acid a white crystalline precipitate is thrown down. On standing, the supernatant liquid deposits very distinct pale yellow tabular crystals. When potassic bromide is added to the sodic solution, a yellow oil separates after a time, which dries to a pale yellow gummy transparent mass. Of this salt,

0.9284 gram lost over a radiator 0.0595 gram = 6.41 per cent.
0.9492 gram gave 0.0822 gram As_2O_3 with iodine = 8.65 per cent.
1.2191 gram gave 0.1061 gram As_2O_3 with iodine = 8.70 per cent.
0.8961 gram gave 0.0944 gram $P_2O_7Mg_2$ = 6.74 per cent. P_2O_5.
0.8916 gram gave 0.6458 gram $P_2O_5 + WO_3$ = 72.43 per cent.
0.8916 gram gave 0.5064 gram $PtCl_6K_2$ = 11.03 per cent. K_2O.

The formula which best represents the analyses is

$$12WO_3.2As_2O_3.2P_2O_5.5K_2O.Na_2O + 15Aq,$$

which requires:

		Calculated.	Found.	
$12WO_3$	2784	65.24	65.69	
$2As_2O_3$	396	9.28	8.65	8.70
$2P_2O_5$	284	6.65	6.74	
$5K_2O$	472	11.06	11.03	
Na_2O	62	1.45	1.48	
$15H_2O$	270	6.32	6.41	
	4268	100.00		

The arsenous oxide is too low, but the sum of the arsenous and tungstic oxides, as well as the percentages of the other constituents of the salts, agree well with the formula.

60 : 1 : 4 : 7 *Potassic Arsenoso-phospho-tungstate.*—When a solution of potassic phosphate is poured into one of sodic arsenoso-tungstate as prepared by boiling arsenous oxide with 12 : 5 sodic tungstate, no precipitate is formed; but on adding chlorhydric acid the liquid becomes yellow, and, after standing, deposits beautiful pale yellow crystals. For analysis these were washed with cold water and dried on woollen paper. The salt is soluble in hot water, but appears to be decomposed by solution. In this salt,

1.2498 gram gave 0.0671 gram $P_2O_7Mg_2$ = 3.43 per cent. P_2O_5.

1.2587 gram gave 0.0151 gram As_2O_3 by iodine = 1.20 per cent.

1.0348 gram gave 0.9192 gram $WO_3 + P_2O_5$ = 88.81 per cent.

1.3143 gram lost over a radiator 0.0787 gram = 5.99 per cent. water.

The analyses correspond closely to the formula

$$60WO_3.As_2O_3.4P_2O_5.7K_2O + 55Aq,$$

which may also be written

$$60WO_3.2AsO_3H_3.4P_2O_5.7K_2O + 52Aq.$$

The formula requires:

		Calculated.	Found.
$60WO_3$	13920	85.21	85.38
$4P_2O_5$	568	3.48	3.43
As_2O_3	198	1.21	1.20
$7K_2O$	661	4.04	4.00 (diff.)
$55H_2O$	990	6.06	5.99
	16337	100.00	

It is of course very possible that this may be a double salt, but there are at present no data upon which we can base a rational distribution of the components.

ARSENOSO-ARSENIO-TUNGSTATES.

The salts which belong to this group are formed under the same conditions as the corresponding arsenoso-phospho-tungstates. They are in many cases highly crystalline and well defined, and appear to be very numerous.

Analytical Methods.—Arsenic acid may be directly determined in the soluble salts of this series by means of magnesia-mixture, but it is best to redissolve the precipitated ammonio-magnesic arsenate in chlorhydric acid, and precipitate a second time by ammonia. Arsenous oxide may be determined by titration with iodine after adding an excess of an alkaline dicarbonate. As a check upon the determination of the two oxides of arsenic, it is well to oxidise a portion of the salt directly by means of nitric acid, and then determine the total arsenic oxide by means of magnesia-mixture. A further check may also be obtained by reducing the arsenic oxide by boiling with sulphurous acid, and then titrating the total arsenous oxide by means of iodine. In solutions from which the arsenic has been completely removed as As_2S_3, tungsten can be determined by means of mercurous nitrate, provided that no chlorhydric acid or chloride is present.

21 : 1 : 4 : 10 *Potassic Arsenoso-arsenio-tungstate.*—When potassic bromide is added to a solution of arsenoso-tungstate of soda, and a solution of potassic arsenate, AsO_4K_2H, is then poured into the clear filtrate, a white crystalline precipitate is formed. This salt requires a very large quantity of hot water for solution. Baric chloride boiled with it gives a well-defined flocky-crystalline salt. Argentic nitrate gives a similar salt, but this has a faint tinge of fawn-color, perhaps due to the presence of a trace of potassic arsenate not completely removed by washing. Mercurous nitrate gives on boiling a clear yellow flocky-crystalline salt. In the potassic salt,

1.9985 gram gave 0.3468 gram $As_2O_7Mg_2$ = 12.36 per cent. As_2O_5.

2.0085 grams gave 0.0527 gram As_2O_3 by iodine = 2.62 per cent. As_2O_3.

After complete oxidation by nitric acid,

1.5004 gram gave 0.3162 gram $As_2O_7Mg_2$ = 15.63 per cent. As_2O_5.

1.9684 gram gave 1.2935 gram WO_3 = 65.72 per cent.

1.5825 gram gave 1.0346 gram WO_3 = 65.37 per cent.

1.3890 gram gave 0.9382 gram $PtCl_6K_2$ = 13.09 per cent. K_2O.

1.5765 gram lost over a radiator 0.0955 gram = 6.06 per cent.

The analyses lead to the formula

$$21WO_3.As_2O_5.4As_2O_5.10K_2O + 26Aq,$$

which requires:

		Calculated.	Found.	
$21WO$	4872	65.86	65.72	65.37
As_2O_3	198	2.68	2.62	
$4As_2O_5$	920	12.43	12.36	
$10K_2O$	940	12.70	13.09	
$26H_2O$	468	6.33	6.06	6.39 (diff.)
	7398	100.00		

Of course, in these salts, as in the arsenoso-phospho-tungstates described, arsenic may be supposed to be in the form of $[H.AsO.(OH)_2]$ either wholly or partially.

Classes of antimonoso-arsenio-tungstates, antimonoso-antimonio-tungstates, and arsenoso-antimonio-tungstates, appear also to exist and to be formed by processes exactly analogous to those described in the cases of the compounds containing two oxides respectively of the forms R_2O_3 and R'_2O_5, united with tungstic oxide.

(*To be continued.*)

SOME EXPERIMENTS ON THE QUANTITATIVE EFFICIENCY OF THE MARSH-BERZELIUS METHOD FOR THE DETECTION OF ARSENIC.

By W. P. Headden and B. Sadler, Jr.

We were led to make this investigation by the following observations: 1st. That when a solution containing a small quantity of arsenic is brought into the evolution flask of a Marsh apparatus, the evolution of arseniuretted hydrogen is copious and regular for a short time, but it then diminishes very rapidly, and will often give no mirror after the lapse of twenty minutes; 2d. That when the evolution is slow and regular, and the decomposition chambers are together not less than three inches long, and that portion of the tube in which the deposition of the arsenic is to take place is sufficiently narrow and long, no arsenic escapes, either by being

carried forward and out of the tube mechanically, or in the form of arseniuretted hydrogen.

It is stated that in the detection of arsenic by means of Berzelius' modification of Marsh's method, enough arseniuretted hydrogen always escapes to give arsenic spots on porcelain. We find this to be true whenever the evolution of hydrogen is rapid, or the quantity of arseniuretted hydrogen is relatively very large, and the temperature of the decomposition chamber is not proportionately increased. If the evolution of hydrogen is too rapid, arseniuretted hydrogen, though present in relatively small quantities, may escape decomposition in chambers of the length given, even though they are kept at a dull red heat. We found it necessary in our experiments so to regulate the evolution of the hydrogen that it burnt with a flame not exceeding 5–6 mm. when issuing from an opening of about 1 mm. diameter.

Two grams of resublimed arsenious acid were dissolved in a sodic carbonate solution, and the solution diluted to 1 litre. The following determinations were made with this solution:

	Quantity of Sol. used.	Duration of the feeding.	Per cent. of As found.	Duration of Experiment.
1.	50 cc.	45 min.	98.80	2 hrs. 00 min.
2.	"	"	98.99	2 hrs. 30 min.
3.	"	"	98.56	4 hrs. 30 min.
4.	"	"	98.94	2 hrs. 30 min.
5.	"	55 min.	99.26	2 hrs. 30 min.

In experiment 3, the evolution of gas was so rapid and irregular at the beginning that a portion of the arseniuretted hydrogen escaped decomposition and was lost. The solution was fed through a burette, and the gas was dried by being passed over calcium chloride. In some experiments made previous to those recorded we used soda-lime as a dryer, with results varying from 91.60 per cent. to 94.30 per cent. of the arsenic present. The soda-lime was examined and found to contain arsenic. We attributed the low results to the action of the caustic alkali on the arseniureted hydrogen, and substituted pure calcium chloride for the soda-lime. In each of the five experiments given above we used a fresh portion of calcium chloride; because we noticed that when the same calcium chloride was used in more than one or two experiments, or until it had become coated with its aqueous solution, arseniureted hydrogen seemed to be retained, and our results correspondingly lowered.

In one series of experiments in which the same calcium chloride was used four times we obtained the following results: 1st. 98.94 per cent.; 2d. 97.75 per cent.; 3d. 96.36 per cent.; 4th. 94.51 per cent. In two others in each of which the calcium chloride was used three times we obtained: 1st. 99.26 per cent.; 2d. 98.70 per cent.; 3d. 98.20 per cent. in one series, and, 1st. 98.94 per cent.; 2d. 95.00 per cent.; 3d. 94.70 per cent. in the other.

A very small drying tube was found to be sufficient. The one used was about 5 cm. long and rather more than 1 cm. in diameter.

In testing the applicability of this method to the determination of arsenic in minerals we selected an arseno-pyrite which had been analysed and found to contain 43.44 per cent. arsenic.

Two grams of this mineral were brought into solution by *aqua regia*, and the solution evaporated down with addition of sulphuric acid, and heated to expel the last traces of nitric acid. After this had been effected the solution was diluted to one litre, and two determinations of arsenic were made, with the following results: 32.15 per cent., 32.60 per cent. We attributed the low result—only 74.08 per cent. of the arsenic present—to the fact that the arsenic was present in the form of arsenic acid. One-half litre of the solution was taken and the arsenic acid reduced to arsenious by boiling with a solution of sulphurous acid. Four determinations were made with this solution, giving us 36.90 per cent., 37.55 per cent., 37.25 per cent. and 37.00 per cent. A subsequent determination, made from another sample treated in the same manner, gave 36.80 per cent. arsenic. The last solution differed from the solution of arsenious acid in that it contained a salt of iron. A measured portion of the solution precipitated with sulphuretted hydrogen, and a solution of arsenious acid prepared by dissolving the arsenic trisulphide in acid sodium sulphite, with subsequent addition of sulphuric acid, and boiling to expel all sulphur dioxide from the solution. Some of the sulphur and arsenic trisulphide which separated out did not redissolve in this solution; it was filtered off and brought into solution in another portion of acid sodium sulphite. The solutions were united and boiled with a slight excess of sulphuric acid. The solution remaining clear, it was supposed that all the polythionates had been destroyed, but the solution gave a precipitate of sulphur and arsenic trisulphide when brought into the evolution flask, and arsenic trisulphide was deposited in the tubes. The rest of the solution (200 cc.) was evaporated down

with the addition of sulphuric acid. It remained clear until it had been reduced to less than 50 cc., when a further separation of sulphur and arsenic trisulphide took place. The temperature of the solution was not determined. This precipitate was brought into solution and added to the main portion. Two determinations of the arsenic in this solution gave 41.67 per cent. and 41.53 per cent. arsenic. The arsenic was precipitated from the solution of another sample as the trisulphide, which was brought into solution in fuming nitric acid, evaporated down with sulphuric, and heated to expel last traces of the nitric acid, the arsenic acid reduced by solution of sulphurous acid, and the solution diluted up to 1 litre. Two determinations of the arsenic in this solution gave 41.55 per cent. and 41.52 per cent. of arsenic. We found no difficulty in reducing the arsenic acid in a sulphuric acid solution by means of a strong sulphurous acid solution, the reduction being completely effected within 1½ hours.

The next mineral experimented with was a tetrahedrite. The sample was brought into solution, the arsenic acid reduced and thrown down with the antimony and copper, the antimony and arsenic sulphides were dissolved out and separated by means of acid potassium sulphite. The arsenic was thrown down from this solution by sulphuretted hydrogen, and finally obtained in solution as arsenious acid. Two determinations of arsenic were made with this solution; one gave 4.20 per cent., the other 4.16 per cent. of arsenic.

A second sample was treated in the same manner, and two determinations made with this solution gave 3.81 per cent. and 3.81 per cent. The arsenic in a third portion of this solution was determined as magnesic-pyro-arsenate, and gave 3.801 per cent. of arsenic.

The zinc used was "C. P." bar zinc, but while it was free from arsenic, the amount of carbon contained in the different bars varied greatly, and only a few of them dissolved without any residue. The facts (1) that the presence of about 33 per cent. of iron in the arseno-pyrite reduced the amount of arsenic obtained by more than 10 per cent., (2) that our highest results were obtained with the purest zinc which we succeeded in procuring, (3) that when two experiments were made with the same bar of zinc, one-half of it being used in each, they agreed better than when they were made with different zincs, suggested that the constant deficit in our

determinations, even after we had eliminated other sources of error so far as we could, might be due to the influence, probably galvanic, of the carbon in the zinc. We endeavored to establish this by using some bar zinc which was very rich in carbon. The other conditions of the experiments were the same as in the first series given. The results obtained were 95.8 per cent., 95.2 per cent., 95.05 per cent. of the arsenic introduced into the flask. Another determination was made with the addition of copper sulphate solution, and we obtained 69.30 per cent. of the arsenic. In the early part of our investigation we brought, in some experiments, platinic chloride, in others a spiral of platinum wire, into the evolution flask, and obtained such low results that we rejected them.

In all of these experiments the arsenic was deposited in two tubes; 97 per cent. on an average being deposited in the first tube, and all of the rest in the second. A third tube was used in a number of the experiments, but in no instance was any arsenic obtained in it.

The most convenient tube was found to be a hard glass tube with a total length of 18 cm. The decomposition chamber was 6 cm. long and 1 cm. wide. That portion in which the deposition took place was about 10 cm. long and 6 mm. wide. The second tube was of the same form, but the decomposition chamber need not be more than one-half so long.

Our conclusion is that the method will give satisfactory results under the following conditions:

1st. The zinc must be free from carbon, and pure in other respects.

2d. The arsenic should not be present in the form of arsenic acid.

3d. Iron, copper, platinum or their salts, and probably the other heavy metals and their salts, must be absent.

4th. The calcium chloride should be neutral and should not be used more than once.

5th. The feed and the evolution of the gas should both be slow and regular, and the decomposition chamber kept at a dull red heat.

Contributions from the Chemical Laboratory of Harvard College.

XLVI.—ON THE ACTION OF CHROMIC SUPERFLUORIDE ON BENZOIC ACID.[1]

By C. Loring Jackson and George T. Hartshorn.

As the chromic superfluoride is instantly decomposed by water with the formation of chromic anhydride and hydrofluoric acid, we undertook the experiments described in the following paper in the hope that organic compounds containing hydroxyl would act in a similar way; and since Mallet's[2] determination of the vapor-density of hydrofluoric acid obliges us to assign it the formula H_2F_2, that thus we might obtain organic substances, in which the oxygen of the hydroxyl was replaced by two atoms of fluorine, as in fluosilicic acid. This hope has not been realized in the case of benzoic acid, with which we began our experiments, as the chromic superfluoride left the hydroxyl entirely unaltered; but, on the other hand, it has led us to a very interesting result, as the products of the reaction were chromic fluoride (Cr_2F_6) and a difluorbenzoic acid, and therefore we have achieved for the first time, so far as we can find, the direct substitution of the hydrogen in an organic substance by fluorine. Preliminary experiments with acetic acid and benzol seem to show that the reaction is a general one,—in both cases the chromic superfluoride was reduced to a lower fluoride of chromium,—and there is good promise, therefore, that it will prove of service in adding new members to the class of fluorine organic compounds, as yet so meagrely represented.

We have not made a complete study of the difluorbenzoic acid, but have contented ourselves with doing enough to characterise it thoroughly, as we are anxious to avoid any interference with Paterno, who has already begun the investigation of organic bodies in which hydrogen is replaced by fluorine. Nor do we intend to continue our experiments on acetic acid and benzol, as Paterno has announced that he is at work on the fluorine derivatives of both these substances. We wish, however, to reserve for our future

[1] From the Proceedings of the American Academy. Communicated by the Authors.
[2] This Journal **3**, 189.

study the action of chromic superfluoride on all other organic substances.

The remainder of the paper consists of the detailed account of our experimental work.

Action of Chromic Superfluoride on Benzoic Acid.

The chromic superfluoride was made by the action of 180 grams of fuming sulphuric acid on 60 grams of potassic dichromate and 100 grams of calcic fluoride, both of which must be perfectly dry. If the fuming sulphuric acid is very strong, it should be diluted with ordinary strong sulphuric acid, as, if this precaution is neglected, the action is so violent that it cannot be controlled, a large amount of the superfluoride is wasted, and in extreme cases the cover may be blown off the lead retort. The lead retort used was of the cylindrical form figured in most text-books for making the aqueous solution of hydrofluoric acid; the fuming sulphuric acid was first introduced, the fluor-spar and potassic dichromate previously thoroughly mixed were then added, and stirred in with an iron rod, the cover put on, and the reaction started by a gentle heat. As soon as faint white fumes appear at the exit tube, the lamp should be removed, and, after the first violent evolution of gas has slackened, the action can be made to proceed smoothly by a gentle heat, although it is hard to avoid occasional rushes of gas. It is hardly necessary to say that the work should be carried on under a good hood, and the hands protected by india-rubber gloves. After the process is finished, the retort should be emptied before it has become cold, as after the residue has hardened its removal is both difficult and tedious.

The chromic superfluoride obtained in this way is not free from hydrofluoric acid, to judge from the white fumes which were observed mixed with the dark red heavy vapor; but it was pure enough for our purpose, and was allowed to act directly on the solid benzoic acid, which was spread in a layer rather less than a centimeter thick over the bottom of a platinum dish, or on its cover; for this purpose the lead pipe, which formed the exit tube of the retort, was brought down so that it nearly touched the surface of the acid. Absolute contact must be avoided, as in this case the tube soon becomes stopped up with the fused product. With a rapid stream of the superfluoride the action is vigorous,

the benzoic acid fusing and forming a black crust, which was made to spread over the whole surface by moving the dish when necessary; the crust was then removed,[1] and the same action repeated with fresh benzoic acid, until all the superfluoride was exhausted. In this way 180 grams of the crusts could be obtained in a single operation. If the stream of superfluoride was not rapid, the benzoic acid was apt to become covered with chromic anhydride, probably from a trace of moisture in the acid, and this not infrequently gave rise to unimportant deflagrations; but the amount of chromic anhydride formed even by this secondary reaction is very small, almost the whole of the chromic superfluoride being converted directly into the green chromic fluoride Cr_2F_6.

To obtain the difluorbenzoic acid from the crude product it was dissolved in a strong solution of sodic carbonate, and, after the chromic hydrate had been removed by filtration, fractionally precipitated with hydrochloric acid, the liquid being boiled with the separated benzoic acid after each precipitation. We found it wisest to divide the whole into two about equal fractions at first, and then to fraction the least acid portion again, when all the difluorbenzoic acid collected in the least acid fraction, which should be made very small; this was then boiled with water, and the residue purified by recrystallisation from boiling benzol and sublimation. The yield of difluorbenzoic acid is only 1.5 per cent. of the benzoic acid used.

Having obtained the difluorbenzoic acid, we next tried to detect the presence of monofluorbenzoic acid, and for this purpose examined the acid contained in the hot aqueous filtrate from boiling the difluor acid with water, and also the fraction immediately preceding the least acid one. As the metafluorbenzoic acid melts at 123°–124° according to Paternò and Oliveri,[2] the melting-point was of no assistance to us, and we have accordingly made a number of analyses of the barium salts of these fractions, both before and after a repetition of the fractional saturation, which have given results varying from 35.81 to 35.99 per cent. of barium; baric benzoate contains 36.15 per cent., baric fluorbenzoate 33.01 per cent.[3] We also thought it might be contained in a mixture of acids, obtained by boiling the crude product with insufficient

[1] We think it right to mention that both of us were poisoned, one severely, by the crude product, which was spilt on our clothes in removing the crusts from the platinum dishes.

[2] Ber. d. ch. G. **15**, 1197.

[3] The most acid fractions were also pure benzoic acid, as was to be expected.

water, melting sometimes as low as 102°; but this on fractional neutralisation was divided into difluorbenzoic acid and benzoic acid, as proved by analyses of the barium salt. We are convinced, therefore, that no monofluorbenzoic acid is formed by the action of chromic superfluoride on benzoic acid, but the products of the reaction are only difluorbenzoic acid and chromic fluoride with a little chromic anhydride as an impurity.

Difluorbenzoic Acid $C_6H_3F_2COOH$.

The acid prepared and purified, as described above, appears when sublimed in white flattened needles looking very much like benzoic acid, when crystallised from alcohol or benzol in short fine needles; it sublimes at a temperature far below its melting-point, 232° (uncor.), but with much more difficulty than benzoic acid, and burns with a strongly green-bordered flame. It is essentially insoluble in cold water, and only slightly soluble in hot, the boiling solution depositing a few crystalline flocks of the acid on cooling; not very freely soluble in cold alcohol or benzol, but freely in either of these solvents when hot, very soluble in ether or glacial acetic acid, less so in methyl alcohol, and almost insoluble in ligroine, or carbonic disulphide. Benzol is the best solvent for purifying it by crystallisation.

Its composition was established by the following combustions:

I. 0.2549 gram of substance burnt with plumbic chromate in a closed tube[1] gave 0.4964 gram of carbonic dioxide and 0.0982 gram of water.

II. 0.1595 gram gave 0.3131 gram of carbonic dioxide and 0.0506 gram of water.

	Calculated for $C_7H_4F_2O_2$.	Found. I.	Found. II.
Carbon	53.16	53.13	53.52
Hydrogen	2.53	4.28	3.53

The ammonic difluorbenzoate is decomposed by evaporating its solution to dryness; but a solution freed from ammonia by boiling gave white precipitates with plumbic acetate, and mercurous, mercuric and argentic nitrates, and a bluish white precipitate with cupric sulphate.

[1] We found it impossible to obtain agreeing results when the combustion was performed in the ordinary way with oxygen.

Baric Difluorbenzoate, $Ba(C_7H_3F_2O_2)_2$, made by boiling the acid with baric carbonate and water, crystallises in white scales, and contains no water of crystallisation even when only air-dried.

I. 0.2716 gram of the salt dried at 110° gave 0.1395 gram of baric sulphate.

II. 0.2674 gram gave 0.1378 gram of baric sulphate.

	Calculated for $Ba(C_7H_3F_2O_2)_2$.	Found. I.	II.
Barium	30.38	30.20	30.28

Its solubility in water was determined according to the method of Victor Meyer:

I. 1.5814 gram of a solution saturated at 15° gave 0.0188 gram of the salt by evaporation.

II. 2.6260 grams gave 0.0310 gram of the salt.

Therefore, the solution saturated at 15° contains the following percentages of the salt:

I.	II.
1.19	1.18

Calcic Difluorbenzoate, $Ca(C_7H_3F_2O_2)_2.3H_2O$.

This very characteristic salt, made by boiling the acid with calcic carbonate and water, begins to crystallise out, as soon as the liquid is somewhat concentrated, in bundles of silky needles, frequently a centimeter long, and slightly branched at a very acute angle.

I. 0.7886 gram of the air-dried salt lost 0.1058 gram at 100°.

II. 0.3605 gram lost 0.0495 gram.

	Calculated for $Ca(C_7H_3F_2O_2)_2.3H_2O$.	Found. I.	II.
Water	13.28	13.42	13.73

I. 0.2440 gram of the salt dried at 100° gave 0.0914 gram of calcic sulphate.

II. 0.3024 gram gave 0.1153 gram of calcic sulphate.

	Calculated for $Ca(C_7H_3F_2O_2)_2$.	Found. I.	II.
Calcium	11.30	11.02	11.21

Its solubility in water was determined according to the method of Victor Meyer:

I. 2.0134 grams of a solution saturated at 15° gave 0.0100 gram of the anhydrous salt by evaporation.

II. 5.1731 grams gave 0.0256 gram of the anhydrous salt.

Therefore, the solution saturated at 15° contains the following percentages of the anhydrous salt:

I.	II.
0.50	0.49

The calcium salt when heated with an excess of lime gives off a combustible vapor, probably difluorbenzol, as only 4 per cent. of fluorine was removed from the acid in this way, but we do not intend to try to isolate this product for fear of interfering with Paterno. This observation was made in an attempt to determine the fluorine in the acid by Piria's method,[1] which showed that a much larger layer of alkali than could be obtained in this way was needed to remove the fluorine from the organic compound. We propose in our subsequent work to make another effort to solve this difficult problem in organic analysis.

It is to be observed that the large percentages of hydrogen obtained in the combustion of the acid correspond to the formula $C_6H_3F_2CO_2H$ better than to $C_6H_2F_2CO_2H$, and that our other analytical work is not capable of deciding between these formulas. The formula $C_6H_5F_2CO_2H$ would be that of an oxybenzoic acid containing two atoms of fluorine instead of one of oxygen $\left(\begin{matrix}C_6H_4COOH\\F_2H\end{matrix}\right)$, and although the difficulty of removing the flourine from the acid rendered this formula highly improbable, we have thought it necessary to prove that it was incorrect. For this purpose we treated the acid with a large excess of potassic hydrate in alcoholic solution, and analysed the potassium salt, which can be precipitated by ether in broad silvery scales, when we obtained an amount of potassium corresponding to the formula $C_6H_3F_2CO_2K$.

[1] H. Schiff, Ann. Chem. **195**, 293.

NOTES ON THE EXTRACTION OF VANADIUM FROM MAGNETITE; ON THE CONDUCT OF SEVERAL COMPOUNDS OF VANADIUM TOWARDS REAGENTS; ON ITS QUANTITATIVE DETERMINATION; AND ITS SEPARATION FROM CHROMIUM.

By Edo Claassen.

1. By igniting finely pulverised and bolted magnetite with saltpetre (about ⅓ or ½ its weight) it is not decomposed. Even if this operation be repeated several times, until after extraction with hot water all the vanadium present is found in the filtrate the central part of the exceedingly minute grains of the ore is still magnetic, and has escaped oxidation.

2. If magnetite is digested for a long time with warm concentrated hydrochloric acid, it is in proportion to the purity of the ore more or less dissolved. The insoluble part then remaining is decomposed by igniting with saltpetre and soda. The mass taken from the crucible is mixed with the acid solution, from which most of the free hydrochloric acid has been previously evaporated. Some saltpetre is now added, and also, if necessary, some sodium carbonate, enough to give the acid solution a strongly alkaline reaction, after which the whole is evaporated to dryness, and kept red-hot for some time in an iron crucible. The contents of the crucible lixiviated with water furnish a liquid which contains *all* the vanadium (and also all the chromium) present in the ore, and from which it is separated as usual by barium chloride in form of barium vanadate.

3. Vanadium oxide, prepared by precipitating the green solution of vanadic acid in hydrochloric acid by ammonia, *cannot* be entirely dissolved in ammonium sulphide, even if the digestion with it is several times repeated.

4. Its solution is, however, easily effected by melting it in a covered porcelain crucible (if necessary, repeating this operation with the residue which sometimes remains after extraction with hot water) with six times its weight of equal parts of sulphur and sodium carbonate.

5. From the solutions thus obtained (see 3 and 4) it is impossible to precipitate in one operation all the vanadium by acetic, chlor-

hydric or sulphuric acid with or without the aid of heat. The bluish-green color of the filtrate is caused by some vanadium still present. If, however, the filtrate is neutralised or made alkaline and then mixed with ammonium sulphide and one of the above acids, some vanadium, but not all, is again precipitated as sulphide. By repeatedly (say six to ten times) operating in this way the vanadium is separated so far that only traces of it can be detected in the liquid (see 15).

6. Vanadium sulphide, ignited either with access of air for a long time, or after having been moistened with concentrated nitric acid or a solution of ammonium nitrate, leaves vanadic acid, but always mixed with some oxide. By extracting this residue with a solution of ammonium carbonate or with ammonia, the oxide is left undissolved.

7. Vanadium oxide, treated like the sulphide (see 6) leaves the vanadic acid also mixed with some oxide.

8. Ammonium vanadate, when ignited, leaves vanadic acid. This generally contains, however, a small quantity of oxide to be separated from the acid as above (see 6).

9. A colorless or faintly yellowish solution of ammonium vanadate turns yellow by being exposed to the air for some time. It has lost some ammonia, an addition of which will after heating restore the original color.

10. If vanadic acid is to be separated by means of ammonium chloride from a solution containing ammonium vanadate, care should be taken that this solution is colorless or nearly so, has a neutral or faintly alkaline reaction, or that if yellow, it be heated with some ammonia in order to get such a solution. For it should be remembered that in a yellow solution there will always be formed, besides the usual white or yellowish deposit, a yellow one, which, when being washed with a saturated ammonium chloride solution, will redissolve again with yellow color, thus causing a considerable loss of vanadic acid. For this reason a liquid containing the potassium or sodium salt should, after addition of ammonium chloride, not be allowed to stand in the open air much longer than necessary to precipitate all the ammonium vanadate. If the yellow deposit is formed, however, the liquid only needs heating with a little water and ammonia to make it fit for a new addition of ammonium chloride. If a chromate, however, is present in the solution together with a vanadate, it is evident that the liquid

will always be more or less yellow, even when having an alkaline reaction. In this case notice has to be taken of the alkaline reaction only, which suffices to indicate that the solution is fit for an addition of ammonium chloride.

11. Although the use of ammonium chloride is frequently recommended as a means of exactly determining the quantity of vanadic acid present, it seemed to me, as some vanadic acid was occasionally found in the filtrate, to be well worth while to make some experiments on this subject. These indicated positively that a small amount of the vanadate always enters the filtrate, from which it can be separated by alcohol. On redissolving this precipitate in a little water and adding some ammonium chloride, almost all the vanadate is separated, so that only traces are lost.

12. All vanadic acid present in a neutral solution can be separated by means of lead acetate. The lead vanadate formed can be perfectly decomposed by digestion with a mixture of chlorhydric acid and alcohol. The filtrate from the lead chloride formed is entirely free from lead when a sufficient quantity of alcohol is added. After the distillation of the alcohol and the evaporation of the residue in a platinum dish with addition of some concentrated sulphuric acid to dryness, there remains after ignition, all the vanadic acid present, mixed, however, with some oxide. Instead of decomposing the precipitate in this way, the method described under 19 can often be used with advantage.

13. From neutral solutions of the vanadates all vanadic acid is precipitated also by barium chloride. By boiling the precipitate of barium vanadate with dilute sulphuric acid it *cannot be entirely decomposed.* By mixing the dry precipitate with some potassium bisulphate and igniting, decomposition takes place so perfectly that after extraction with water not a trace of vanadic acid is left with the residue of barium sulphate. The solution obtained may be precipitated with a small excess of lead acetate, and the lead vanadate formed (besides lead sulphate) be decomposed as described under 12.

14. If a mixture of barium vanadate and barium sulphate is digested with hydrochloric acid, or with a mixture of the latter and alcohol, a considerable part of the vanadium will enter the bluish-green solution, while some will be retained in the residue on the filter. Treatment with concentrated nitric acid seems to have no effect on this residue.

15. It has been recommended for the quantitative determination of vanadium to precipitate it from a solution of the chloride, previously saturated and reduced by sulphuretted hydrogen gas, by an addition of mercuric chloride and ammonia. Experiments made in this way gave bad results, as even by repeated precipitation it was possible to separate but a small portion of the vanadium from the solution.

Experiment 1.—0.086 gram of vanadic acid was dissolved in concentrated hydrochloric acid, the solution diluted, saturated with sulphuretted hydrogen gas, and mixed with a small excess of the above reagents. The precipitate contained but 0.007 gram of vanadic acid. The same operation twice repeated furnished an equal amount, so that out of the 0.086 gram taken, 0.014 gram only went into the three precipitates, while the balance, 0.072 gram, remained dissolved in the filtrate.

Experiment 2.—Another quantity of vanadic acid was dissolved in hydrochloric acid, and treated, etc., as above. The first precipitate furnished 0.006 gram of vanadic acid only, while the two next ones gave 0.150 gram. Some vanadium still remained in the filtrate; it was repeatedly precipitated as sulphide (see above under 5). The three first precipitates gave 0.052 gram of vanadic acid, and the four next ones 0.014 gram (all, however, containing some oxide), while the filtrate now contained but a very small amount of vanadium—hardly more than a trace.

16. Vanadic acid or oxide, melted with soda and saltpetre, produces a colorless mass which, with water, gives a colorless solution. If, however, chromic oxide, even in small quantity, is present, the color of the melted mass is more or less yellow, according to the quantity of the oxide, as is also that of the solution of the mass.

17. In consequence of the fact that from the solution of an alkaline vanadate not the total amount of vanadic acid is separated by ammonium chloride, an exact quantitative determination by one operation is impossible in this way (see 11). The balance remaining in the filtrate, if not separated as described in 11), will evidently, if chromium oxide is also present, increase the weight of the chromium precipitate separated afterwards.

18. From a mixture of vanadic acid and chromium oxide concentrated hydrochloric acid will by digestion extract the greater part of the vanadic acid, while traces only of chromium oxide

enter the solution. At one trial 0.083 gram of such a vanadic acid left after digestion 0.030 gram, from which, after having been moistened with concentrated nitric acid and ignited by a repeated digestion with hydrochloric acid, but 0.001 gram was extracted. The undissolved 0.029 gram was then melted with soda and sulphur (see 4), by which operation 0.010 gram more of vanadic acid was separated, so that the treatment with concentrated hydrochloric acid left 15.64 per cent. of the vanadic acid with the chromium oxide. It was, however, stated that the original mixture of vanadic acid and chromium oxide contained also some vanadium oxide. On account of this fact there seems to be the possibility that all the undissolved 15.64 per cent. were solely due to the vanadium oxide, in which case concentrated hydrochloric acid would certainly furnish a good means of separating vanadic acid from chromium oxide. Further experiments made on this matter would without doubt be well worth trying.

19. If a mixture of vanadic acid or oxide and chromium oxide is melted with six times its weight of soda and sulphur in a covered porcelain crucible (which operation may be once repeated, if there is a remnant on the filter after extraction with water), and the melted mass treated with hot water, all the vanadium present is found in the solution, while all the chromium remains on the filter as oxide. The solution of the sulphovanadate is heated in a covered beaker glass for a longer time with a small excess of nitric acid; then some soda is added to make the reaction alkaline and the heating continued until the evolution of carbonic acid gas has ceased. The contents of the beaker are now brought into a wide porcelain or platinum crucible, evaporated to perfect dryness and melted. The melted mass is lixiviated with hot water, the solution carefully neutralised with acetic acid, and then precipitated with lead acetate. The washed precipitate suspended in water, containing some nitric acid, is decomposed by sulphuretted hydrogen gas, and the filtrate now obtained furnishes after evaporation and ignition all the vanadic acid present.

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NOTES.

Valence of Phosphorus.

Evidence serving to throw light upon the question of the true valence of phosphorus, as well as of other members of the nitrogen group, is of such a character that a well-defined difference of opinion upon it has existed among chemists, one class regarding these elements as trivalent and another as quinquivalent. The former class account for the existence of such substances as phosphorus pentachloride by holding that they are examples of the so-called molecular compounds, *i. e.* that phosphorus pentachloride is the result of combination between a molecule of phosphorus trichloride and one of chlorine; while the latter class admit the existence of unsaturated compounds, of which ammonia, phosphoretted hydrogen and phosphorus trichloride are examples.

The idea of molecular combination in the case of phosphorus pentachloride, for example, is supported by the fact that this substance, when vaporised by itself, shows a density required by a mixture of an equal number of molecules of phosphorus trichloride and chlorine. On the other hand, Würtz has shown that phosphorus pentachloride may be vaporised without decomposition in an atmosphere of phosphorus trichloride. Furthermore, the discovery by Thorpe of phosphorus pentafluoride, a compound stable in the gaseous state, points also to the quinquivalent nature of phosphorus; against this, on the other hand, it has been argued that this substance is merely a stable molecular compound.

The recent investigations of Michaelis and La Coste[1] contribute evidence very decidedly in favor of the quinquivalence of phosphorus.

Were it possible to obtain a compound isomeric with phosphorus oxychloride, and to prove by its method of preparation and properties that its constitution is represented by the formula $Cl_2 = POCl$, in which one of the chlorine atoms is united to phosphorus through the intervention of oxygen, then a decision in favor of the quinquivalence of phosphorus might safely be rendered. Compounds analogous to phosphorus oxychloride and its hypothetical isomer, in which the chlorine atoms of the latter are replaced by phenyl groups, have been prepared and described.[2] One of these, triphenylphosphine oxide, $PO(C_6H_5)_3$, is formed from triphenylphosphine dibromide, and also from triphenylphosphine by processes perfectly analogous to those involved in the production of phosphorus oxychloride from phosphorus penta-

[1] Berichte der deutschen chemischen Gesellschaft **18**, 2118.
[2] *Ibid.* **15**, 803; Annalen der Chemie **229**, 305.

chloride on the one hand, and from phosphorus trichloride on the other; this analogy is made apparent by the following scheme:

Phosphorus pentachloride.	Phosphorus oxychloride.	Phosphorus trichloride.
$P<^{Cl_3}_{Cl_2}$	$P<^{Cl_3}_{O}$	PCl_3
Triphenylphosphorus dibromide.	Triphenylphosphine oxide.	Triphenyl-phosphine.
$P<^{(C_6H_5)_3}_{Br_2}$	$P<^{(C_6H_5)_3}_{O}$	$P(C_6H_5)_3$.

The other compound of the empirical formula, $PO(C_6H_5)_3$, was formed by treating diphenylphosphorus chloride with phenol, thus:

$$(C_6H_5)_2PCl + C_6H_5OH = HCl + (C_6H_5)_2POC_6H_5.$$

This compound is called phenoxyl-diphenyl phosphine. The first of these compounds, triphenylphosphine oxide, is a solid, melting at 153.5° C., and is perfectly indifferent toward bromine, oxygen, sulphur, selenium, benzyl chloride and methyl iodide; while the second, phenoxyl-diphenyl phosphine, isomeric with the first, is a thick oily liquid and readily combines directly with all the above-mentioned elements, and, more than that, forms crystalline addition products with the halogen compounds of the alkalies, thus showing an analogy with the substitution products of phosphoretted hydrogen, or, in other words, possessing the properties of a compound of trivalent phosphorus. The constitution of this second compound can then only be expressed by representing it as a derivative of the hypothetical isomer, $P<^{Cl_2}_{OCl}$ of phosphorus oxychloride.

As a result, therefore, of the study of these two isomeric substances, their methods of formation and their chemical conduct, the conclusion is drawn that phosphorus, and consequently all the other members of the nitrogen group, are to be regarded as quinquivalent, and that all such compounds as correspond to phosphorus trichloride, etc., are to be considered as unsaturated.

W. C. D.

On the Qualitative Detection of Mercuric Compounds.

In the ordinary course of qualitative analysis the black residue of sulphides, from which As, Sb and Sn sulphides have been extracted by NaOH or K_2S, are boiled with dilute HNO_3, when HgS is said to remain behind as a black insoluble residue. In point of fact, instead of being black, this residue may be brown, dark yellow, light yellow or white, according to circumstances, even though it contains Hg, as it should. All I can say definitely of this compound is that it always contains sulphur and also nitric acid, and probably consists of a mixture of HgS and $Hg(NO_3)_2$. There is at least one compound of this kind known, and accordingly it would seem that the formation of some such compound

might be anticipated in such a process as that given above; but it is not noticed in any text-book on qualitative analysis so far as I know. Fresenius states under the reactions for Hg that *concentrated* HNO_3 forms a compound whose formula is $2HgS.Hg(NO_3)_2$, but it certainly appears from my own experiments that compounds of the same kind, but varying composition, are formed on boiling with *dilute* HNO_3, especially if the boiling be protracted. No way is suggested in Fresenius or any other book for deciding whether a yellow or white residue contains HgS, and the pupil will ordinarily think it not worth while to test by the dry way unless the residue is black, as it is advertised to be. A student in my laboratory has accidentally discovered that boiling this yellow or white residue with Na_2CO_3 solution, after careful washing with water, restores the black color. Just how the composition of the residue is changed by this treatment I have not yet ascertained, but the resulting product is dense, jet black and heavy, and probably contains considerable HgS. The nature of this change needs further investigation.

J. TORREY.

LABORATORY OF IOWA COLLEGE, *October* 1, 1885.

The First Work in Pure Chemistry in America.

In a paper by HUGO SCHIFF and R. SESTINI, of Florence, Italy, which recently appeared in the *Annalen der Chemie* (Band 228, S. 72), occurs the following passage which will be of interest to American chemists:

"A compound of arsenious acid with potassium iodide was first described in the year 1830 by J. P. Emmett. He obtained the compound in the form of a white crystalline powder, by adding potassium iodide to very dilute solutions of arsenious acid or potassium arsenite exactly neutralised with acetic acid." . . . .

"The compound has a two-fold interest from the historical standpoint. John Patton Emmett, Professor in the University of Virginia, from its foundation (1825 to 1842), was one of the first teachers of chemistry in the Union. With the exception of a few investigations by Robert Hare and the elder B. Silliman, which pertained rather to analytical, technical and mineralogical subjects, the communication of Emmett belongs to the earliest period of chemistry in North America, where the science has since grown up to a strong, independent life.